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THE PREPARATION AND PROPERTIES OF D2-CARBORANE-SILOXANES.(U)
JUL 75 E N PETERS, C D BEARD, J J BOHAN N00014-72-C-0277
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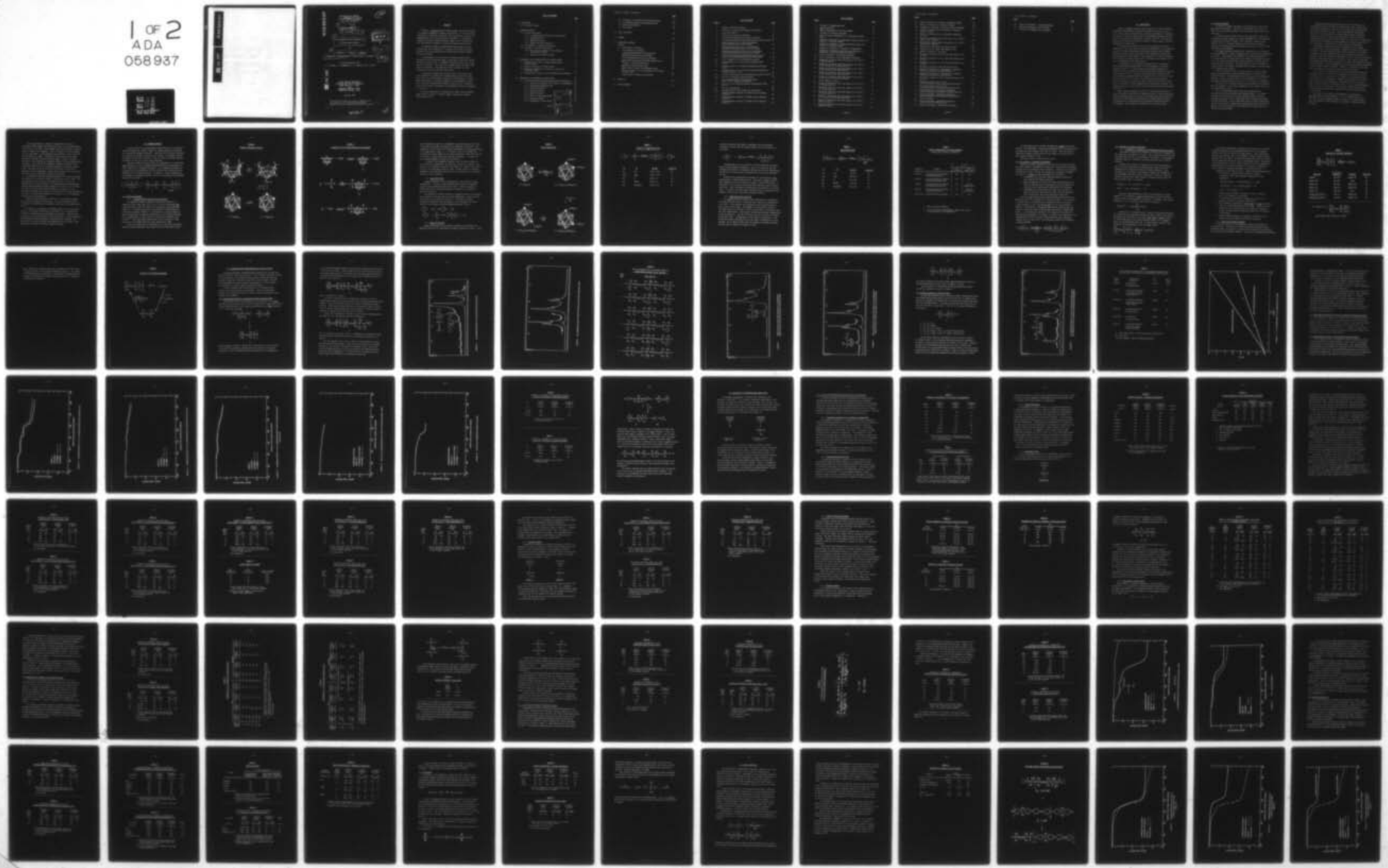

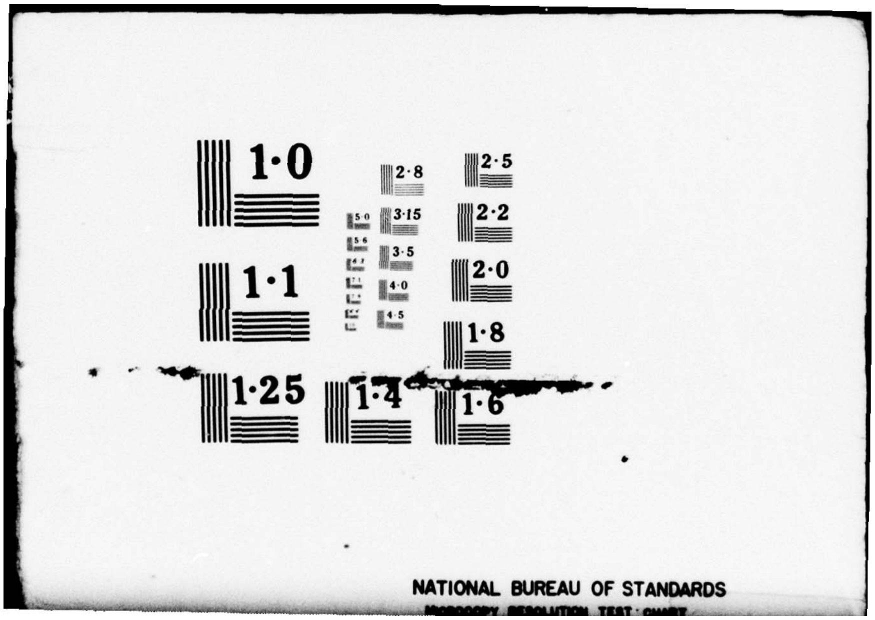
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(12)

OFFICE OF NAVAL RESEARCH
(15) Contract N00014-72-C-0277
Project No. NR 356-525

(9) TECHNICAL REPORT NO. 3

(14) CRL-T-818, TR-3

(6)

The Preparation and Properties of D_2^{m}-Carborane-Siloxanes

By

(11) 31 Jul 75

(10)
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(12) 107p.

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July 31, 1975

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ABSTRACT

UCARSIL, D_2-meta-carborane-siloxane polymer, has been developed for ultrahigh temperature elastomer applications. It offers a unique combination of properties unavailable with fluorocarbon, silicone, or polyphosphazine based high performance elastomers. In particular, UCARSIL has superior thermal stability (300°C in air) in addition to fire and chemical resistance, and good processing characteristics.

An improved synthesis of bis-ureidosilane monomers has been devised which gives >98% purity. A simple and efficient recycling process for recovering m-carborane from unsuitable UCARSIL polymer has been developed.

An investigation of the effects of backbone modifications, extending fillers, molecular weight, and peroxide content was carried out during the past year. Performance correlations exist for a large number of variables. This has led to a highly optimized system which allows exploitation of the potential of the D_2-polymer in high temperature vulcanized elastomer application.

D_2-carborane-methyltrifluoropropyl-siloxane vulcanizates and block copolymers of UCARSIL were characterized. Results show that high levels of trifluoropropyl incorporation are necessary to achieve major improvements in solvent resistance. The attainment of a true block copolymer containing soft UCARSIL blocks fulfills a long-term goal of this program; development of thermoplastic carborane elastomers is continuing.

External evaluations are confirming the unique high performance capabilities of UCARSIL in sealant, gasket, coating and vibration damping applications.

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1.0 INTRODUCTION

UCARSIL, D_2-*meta*-carborane-siloxane polymers, are high performance elastomers having long-term thermal and oxidative stability at 300°C in air.[1] These products singularly meet important requirements in aerospace, military, and electronic applications for elastomeric materials which can survive long periods at temperatures in excess of 260°C.[2] Principal end applications include heat resistant sealants, O-rings, gaskets, coatings, laminates, and molded parts.

Pioneering work carried out at the Olin Corporation[3] under ONR sponsorship in the early 1960's showed that incorporation of the carborane moiety in the siloxane backbone significantly enhanced overall thermal stability; however, serious fabrication and vulcanization difficulties have prevented the exploitation of such materials.[4-6] These difficulties were caused by the harsh conditions of the polymerization reaction which led to a prematurely cross-linked stock.

A new synthesis of D_2-carborane-siloxanes has been developed at Union Carbide which overcomes many of the disadvantages of previous synthetic methods.[1,7] Linear polymers with molecular weights up to 280,000 can now be prepared using silanol-silylurea condensation reactions. Utilizing this process, elastomers with useful general properties and good mechanical properties after heat aging in air at 315°C for 300 hours have been produced.[1,8] Moreover, utilizing data from optimization studies conducted in the past two years, we have achieved marked improvements in performance through formulation and vulcanization changes. The background gained in these studies has facilitated application development activities.

Basic studies relating to the effect of the polymer structure on physical properties, peroxide and extending fillers on thermal stability, and trifluoropropyl moieties on solvent resistance have been carried out. Further, the feasibility of applying the new polymerization process to the preparation of thermoplastic block copolymer elastomers has been demonstrated. These studies are documented in the current report.

1.1 Executive Summary

A significant advance was made in the preparation of high purity bis-ureidosilane monomers. Previously, considerable urea by-product (up to 15%) was generally present; we can now supply material which has >98% purity.

A general synthetic method for the near quantitative conversion of carborane-siloxane polymers (including compounded and cured materials) to m-carborane has been developed. This involves a catalytic, base-induced ($^{-}$OH or F^{-}) cleavage reaction at mild reaction conditions. Recycling by this approach should significantly reduce the cost of using carborane-siloxane polymers.

Four bis-ureidosilane monomers were characterized by differential scanning calorimetry in order to determine their stability at temperatures up to 150°C. The monomers each exhibited an endotherm characteristic of melting and did not reveal any direct evidence of decomposition below 150°. Our newly developed monomer process provided the highest purity bis(ureas) obtained to date. The improved purity of these monomers is a major factor in the greater reproducibility and higher molecular weight of our polymerization process.

Prior utilization of nmr to monitor reactions involving methylphenylsiloxane modification has shortcomings due to overlap of key proton resonances: With experience, this technique has been refined and improved. An nmr technique useful for the preparation of a 33 mole % methylphenylsiloxane modified stock with a M_w of 280,000 is described.

The use of bis-sulfonamide silanes in the preparation of elastomer has been attempted. Side reactions appeared to have adverse effects on the polymerization process.

Five D_2-carborane-siloxane stocks were characterized by differential scanning calorimetry and thermogravimetry. The central siloxane moiety was varied to include dimethylsiloxane, 33 mole % methylphenylsiloxane-67 mole % dimethylsiloxane, methylphenylsiloxane, and diphenylsiloxane. From a relationship between percent modification and the glass transition temperature, methylphenylsiloxane modification appears to be more desirable for suppressing the crystallinity of D_2-carborane-dimethylsiloxane.

Temperature-property relationships and solvent resistance for D_2-carborane-siloxane elastomer were redetermined using a single stock base and the same amount of filler, ferric oxide, and dicumyl peroxide in order to normalize the data. These compounded and cured stocks ($\bar{M}_w$ 250,000) exhibited better low temperature mechanical properties between -20 and -40°C than our previous products ($\bar{M}_w$ stock 100,000). Vulcanizates exhibited TR10 and TR70 values of -38 and -24°C, respectively. The TR70 value correlates with low temperature compression set and TR10 has been found to correlate with brittle points in vulcanizates.

Mechanical properties were also determined for D_2-carborane-siloxane stocks in which the molecular weight was increased from 60,000 to 249,000. The high molecular weight stock was superior in toughness. To supply additional correlative data, the mechanical properties as a function of molecular weight for compounded and cured stocks were determined before and after heat aging at 315°C in air. Before aging, significant performance differences existed, however, the mechanical properties converged after heat aging. It was concluded that molecular weight effects deminished as the crosslink density increased. Further, it appeared that our high molecular weight stocks should be less vulcanized initially.

The effects of extending fillers and antioxidants were evaluated. Extending fillers are large particle additives that reduce the cost of a compound; their use should lower the amount of D_2-carborane-siloxane stock needed in our formulations. Results using Min-U-Sil 5 (30-50 phr) were encouraging in that retention of properties at 300°C was better than a control without this extending filler. The use of finely dispersed ferric oxide as an antioxidant is more efficient than powdered ferric oxide as measured by mechanical properties before and after heat aging in air (315°C).

The effect of the peroxide concentration on the mechanical properties after cure was evaluated. A 1.5 phr concentration of Di Cup R and Vul Cup R appeared optimal for curing. This lower peroxide level has resulted in the elimination of problems in fabricating thick specimens.

Heat aging studies in nitrogen of compounded and cured D_2-carborane-siloxane polymer with and without vinyl cross-linking moieties were carried out at 315°C. Both samples exhibited a decrease in modulus, tensile strength, and elongation. This is indicative of bond breakage in the vulcanizates. A key experiment was performed in which the stock was heat aged in nitrogen. The relative viscosity after heat aging was almost identical to that before heat aging. Clearly, the stock backbone is not undergoing any significant amount of bond cleavage during heat aging. Thus, the loss of mechanical properties observed in the vulcanizates must be due to the thermal breaking of the cross-linking bonds. Heat aging in air at 343° and 371°C showed a rapid loss of properties of the vulcanizates. These results indicate that our material should be rated as a 300-340°C extended use elastomer.

D_2-carborane-methyltrifluoropropylsiloxane stock has been prepared. This material, at a molecular weight of 220,000, has a Tg of -29°C. The trifluoropropyl moiety lowers the thermal stability of the stock. Compounded and vulcanized samples of D_2-carborane-methyltrifluoropropylsiloxane remained elastomeric after aging for 150 hours in air at 290°C. The solvent resistance was improved slightly in comparison to the methylphenylsiloxane stock, however, the results were far from satisfactory. The results do suggest that additional incorporation of trifluoropropyl moieties would be advantageous.

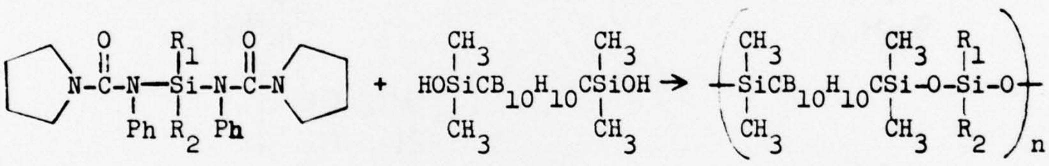
Block copolymers were made consisting of a D_2-carborane-siloxane soft block and a polysulfone hard block. This work demonstrated the feasibility of preparing block copolymers utilizing the UCC polymerization process.

In summary, the preparation of UCARSIL elastomers has been further refined. The variables affecting the performance of a compounded and vulcanized elastomer have been evaluated and optimized. Direction has been given in our search for good solvent resistance. Initial experiments have demonstrated the feasibility of preparing block copolymers. We believe that this work can have broad implications in the field of high temperature elastomers and related polymeric systems.

2.0 MONOMER SYNTHESIS

Current interest in the performance characteristics of D_2-carborane-siloxane polymers has created a demand for larger quantities of material for internal and external evaluation. Therefore, more efficient techniques for preparing the monomer precursors were required. Accordingly, process development studies were initiated in order to optimize existing synthetic procedures, as well as to define new methodology.

The basic UCARSIL process involves the condensation of a substituted bis-ureidosilane, 1, with 1,7-bis-(hydroxydimethylsilyl)-m-carborane, 2, (also referred to as carborane disilanol). Thus, improved procedures for preparing both the ureidosilanes and the disilanol were developed and are discussed in the following sections. In addition, a novel technique for the cleavage of silylated carboranes and for the recycling of the carborane moiety was discovered.



1 2 UCARSIL

2.1 Process Development

2.1.1 1,7-bis-(hydroxydimethylsilyl)-m-carborane

The standard carborane preparation involves the reaction of decaborane with a Lewis base (R_2S or RCN) to form an intermediate bis-ligand derivative which then reacts with acetylene to give o-carborane (Figure 1). Originally, m-disilanol was prepared from m-carborane by a metallation sequence (Figure 2). Unfortunately, the only preparative route to m-carborane of practical significance is the thermal rearrangement of o-carborane in a flow process involving short residence times at 600°C.[9] This vapor phase isomerization is not suitable for large scale work, even though yields are nearly quantitative (98%).

It has been shown that the isomerization of o-carborane derivatives containing large substituted silyl groups at carbon takes place at much

FIGURE 1

STANDARD CARBORANE SYNTHESIS

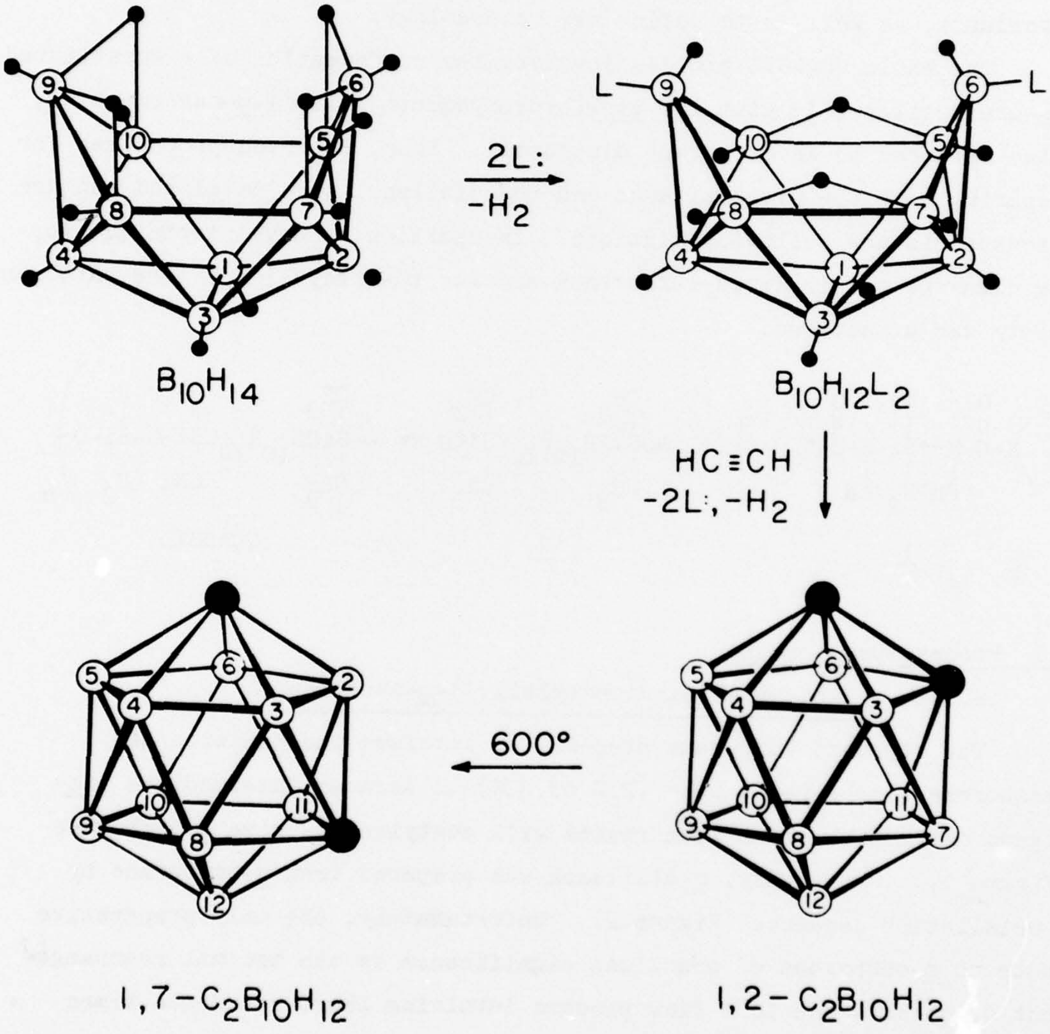
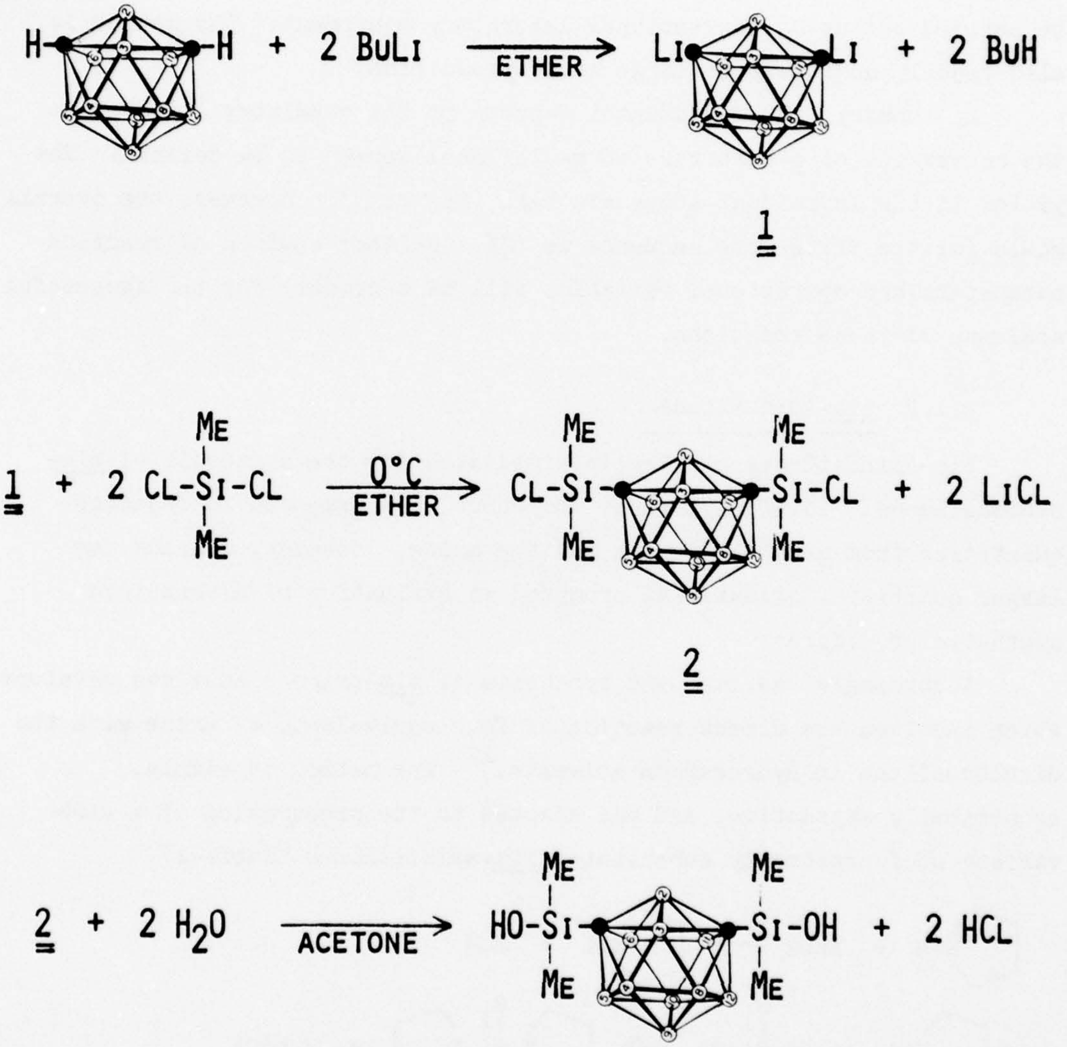


FIGURE 2

SYNTHESIS OF BIS(HYDROXYDIMETHYLSILYL)CARBORANE



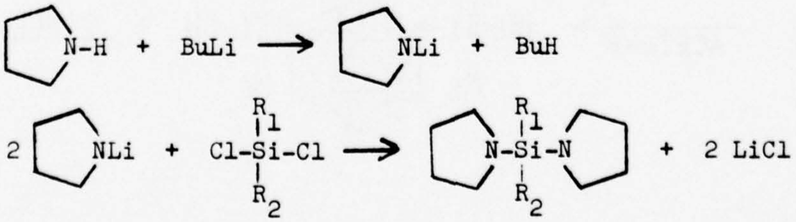
lower temperatures than the rearrangement of o-carborane itself.[10] Thus, an alternative procedure developed at Olin Mathieson Corporation[11] was implemented which involves the thermal rearrangement of o-$C_2B_{10}H_{10}(SiMe_2Cl)_2$ to the meta isomer (Figure 3). In contrast to the flow process, the isomerization occurs readily at the reflux temperature (310-350°C) and can be carried out using conventional laboratory equipment. The method is also readily adaptable to large scale production.

In summary, the fundamental aspects of the chemistry involved in the conversion of o-carborane to m-disilanol appear to be defined. The yields in the individual steps are high (Figure 3); however, the overall yield for the three-step sequence is 67%. Further studies of reaction parameters and operational variables will be necessary for the successful scale-up of these reactions.

2.1.2 bis-Aminosilanes

bis-Aminosilanes are key intermediates for the synthesis of bis-ureidosilanes. Initially, these compounds were prepared in research quantities from n-butyl lithium and the amine. However, demands for larger quantities of material prompted an evaluation of alternative synthetic procedures.

Accordingly, an improved synthesis of bis-aminosilanes was developed which involved the direct reaction of four equivalents of amine with the dichlorosilane in hydrocarbon solvents.[12] The method is simple, economically attractive, and was adapted to the preparation of a wide variety of functionally substituted bis-aminosilanes (Table 1).

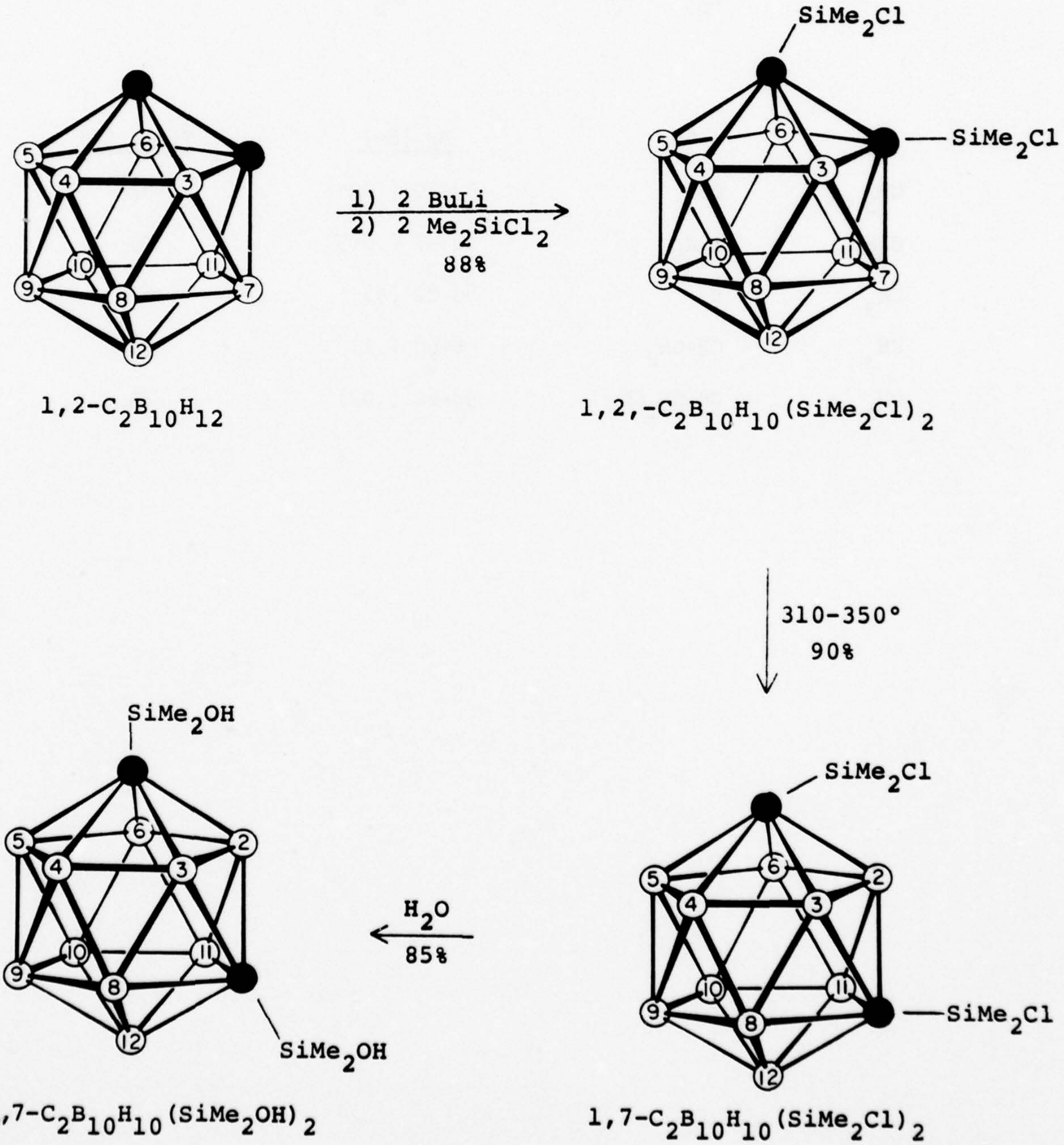


2.1.3 bis-Ureidosilanes

bis-Ureidosilanes are conveniently prepared by the reaction of a bis-aminosilane with two equivalents of phenyl isocyanate in ether. Under

FIGURE 3

BULK ISOMERIZATION



1,2-$C_2B_{10}H_{12}$

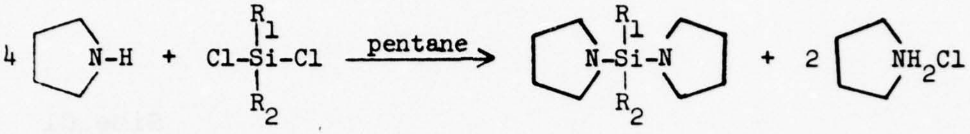
1,2,-$C_2B_{10}H_{10}(SiMe_2Cl)_2$

1,7-$C_2B_{10}H_{10}(SiMe_2Cl)_2$

1,7-$C_2B_{10}H_{10}(SiMe_2OH)_2$

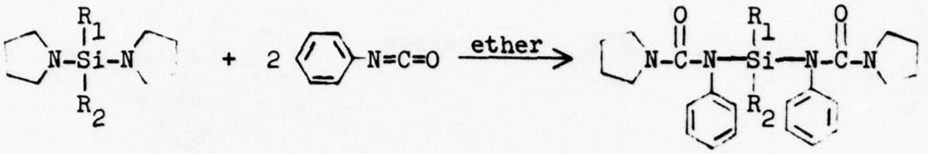
TABLE 1

SYNTHESIS OF bis-AMINOSILANES



R_1	R_2	Bp (mm)	Yield (%)
CH_3	CH_3	59-60 (.025)	87
C_6H_5	C_6H_5	165-7 (.005)	75
CH_3	H	80-82 (4)	61
CH_3	$CH=CH_2$	66-68 (.1)	78
CH_3	$CH_2CH_2CF_3$	58-60 (.02)	75

carefully controlled experimental conditions, the ureidosilanes crystallize directly from the reaction mixture and are collected by filtration.



Ureidosilanes are very sensitive to moisture and must be handled under strictly anhydrous conditions. Thus, it is essential that all reactants and solvents are rigorously purified and that all manipulations are carried out using Schlenk techniques and/or in an inert atmosphere Dry Box.

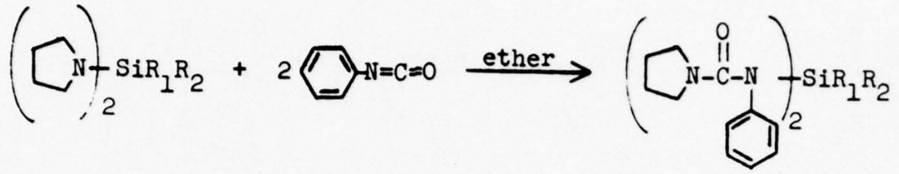
Methods were systematically developed for the synthesis of bis-ureidosilanes in >98% estimated purity. This can be compared with the same compounds which were previously prepared in only 85-88% purity. A combination of nmr analysis and melting point data were used to monitor the purity. Thus, high quality ureidosilanes are available on a routine basis. A variety of ureidosilanes, including several new analogues, were prepared in high purity using these techniques (Table 2).

2.1.4 bis-Ureidosilane Stability

Four bis-ureidosilane monomers were characterized by differential scanning calorimetry (DSC) to determine their stability at temperatures up to 150°C. These monomers were prepared by the old method using n-butyl lithium and an amine. The samples were hermetically sealed in DSC sample pans under nitrogen in a dry box and kept in a desiccator until they were characterized. Each monomer revealed an endotherm characteristic of melting (Table 3) and did not reveal any direct evidence of decomposition below 150°C. The monomers are reluctant to recrystallize. The reluctance towards recrystallizing is most likely characteristic of the monomers, but it might indicate that some change in molecular structure occurred when the monomer was heated to 150°C.

TABLE 2

bis-UREIDOSILANES



R_1	R_2	Mp (°C)	Yield (%)
CH_3	CH_3	124-125	94
C_6H_5	C_6H_5	128-129.5	95
CH_3	H	110.5-113	73
CH_3	$CH=CH_2$	122-124	90
CH_3	$CH_2CH_2CF_3$	131.5-133	93

TABLE 3

MELTING TEMPERATURE OF BIS UREA MONOMERS

(Perkin-Elmer DSC-1B, 10°C/Minute)

Sample No.	Monomer	T_m, °C[1] As Received	T_m, °C[1] Two Weeks Later[2]
579-92-1	bis(N-pyrrolidino-N'-phenylureido)dimethylsilane	108	89
579-53-1	bis(N-pyrrolidino-N'-phenylureido)methylphenylsilane	102	130
579-63-1	bis(N-pyrrolidino-N'-phenylureido)methylvinylsilane	118	did not recrystallize
579-26-1	bis(N-pyrrolidino-N'-phenylureido)diphenylsilane	122	did not recrystallize
10352-102-5	N-pyrrolidino-N'-phenylurea	139	138

1. Peak of melting endotherm.
2. After the original measurements, samples were cooled at 10°C/minute to room temperature.

The methylphenylsilane monomer recrystallized slightly during two weeks at room temperature. The melting temperature after recrystallization was higher than the original value (130 vs. 102°C). The high melting temperature suggests that the material did change its structure when it was originally heated to 150°C.

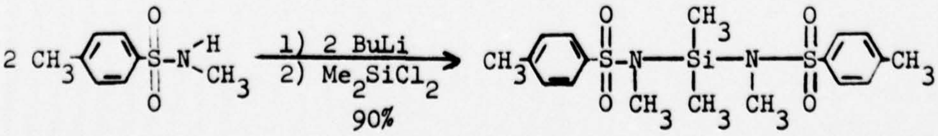
DSC can be used as a quality control test.

2.2 New Monomers - Silylated Sulfonamides

Numerous silylated carboxamide derivatives have received attention as possible monomer intermediates; however, the corresponding sulfonamide analogues have not previously been considered. A search of the literature indicated that little work has been published on silylated sulfonamide derivatives. A priori, several advantages were envisioned:

1. Sulfonamides are accessible starting materials possessing good chemical and thermal stability.
2. Many sulfonamides are soluble in dilute sodium hydroxide and could be removed from the polymerization reaction mixture by extraction and recovered upon acidification for recycling.
3. Sulfonamides are considerably less basic than the urea by-product and may be less likely to enter into side reactions, thus allowing more vigorous polymerization conditions.

Therefore, bis-(N-methyl-p-toluenesulfonamido)dimethylsilane was prepared as shown for evaluation as a potential monomer. As in the case of ureidosilanes, the compound was a crystalline solid, mp 158-162°C. A small quantity (~1-2%) of p-$MeC_6H_4SO_2NHMe$ was the only detectable impurity. Qualitatively, the bis-sulfonamidosilane appeared much less sensitive to moisture than the ureidosilanes and could be handled more easily. In an exploratory experiment, the compound was stirred with excess m-$C_2B_{10}H_{10}(SiMe_2OH)_2$ in benzene. No reaction was observed at room temperature in 24 hours, but the starting materials were completely consumed after 12 hours at 80° with essentially quantitative formation of p-$MeC_6H_4SO_2NHMe$.



2.3 Cleavage of Silylated Carboranes

2.3.1 Nucleophilic Cleavage of the Carborane Carbon-Silicon Bond

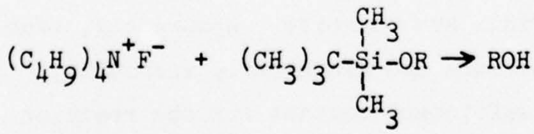
The chemical reactivity of carborane C-H bonds can be compared with the reactivity of acetylenic C-H bonds. Thus, acetylenic derivatives are reasonable model systems for predicting the properties of the analogous carborane compounds. Therefore, silylated acetylenes are of obvious interest.

Ethynyl-silicon bonds are readily cleaved by aqueous alkali, as well as by other nucelophiles, regenerating the parent acetylene.[13] Relatively basic reaction conditions are usually employed. Since carboranes are susceptible to nucleophilic attack, with degradation of the icosahedral cage under similar conditions,[14] clearly, a mild and selective reaction which would cleave the carborane-silicon bond, but leave the cage intact, is required.

$$R'C{\equiv}CSiR_3 + {}^-OH \longrightarrow R'C{\equiv}C^- + R_3SiOH$$

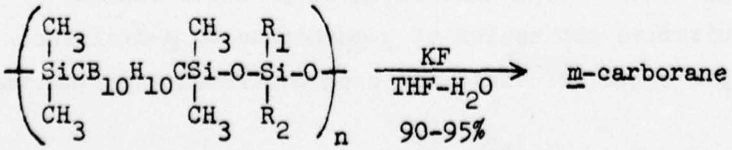
$$R'C{\equiv}C^- + H_2O \longrightarrow R'C{\equiv}CH + {}^-OH$$

Recently, tetrabutylammonium fluoride was introduced as a mild reagent for the cleavage of <u>tert</u>-butyldimethylsilyl ethers in dipolar aprotic solvents under anhydrous conditions.[15] Therefore, under certain conditions, F^- is a strong base and a potent nucleophile.



$$(C_4H_9)_4N^+F^- + (CH_3)_3C\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}OR \rightarrow ROH$$

Subsequently, we discovered that a variety of silylated carboranes, including cured and compounded carborane-siloxane polymers, were smoothly and selectively converted to the parent <u>ortho</u>, <u>meta</u>, or <u>para</u> carborane in nearly quantitative yield using potassium fluoride in a two-phase system of tetrahydrofuran and water. A phase transfer catalyst[16] was convenient for transporting F^- into the organic phase.



$$\left(\overset{CH_3}{\underset{CH_3}{Si}}CB_{10}H_{10}C\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}\overset{R_1}{\underset{R_2}{Si}}\text{-}O\right)_n \xrightarrow[\text{THF-H}_2\text{O} \quad 90\text{-}95\%]{\text{KF}} \underline{m}\text{-carborane}$$

The general experimental conditions are as follows: the silylated carborane was dissolved in tetrahydrofuran (10% w/v) and an aqueous solution of $KF \cdot 2H_2O$ was added in a single portion. With stirring and cooling in an ice bath, two or three drops of a phase transfer catalyst (Adogen 464[17]) were added. The reaction mixture was stirred for 12 hours at room temperature and worked up in a conventional manner. Evaporation of the solvent gave a viscous residue from which the solid carborane was isolated directly by vacuum sublimation. The results of experiments using a variety of silylated carboranes are outlined in Table 4.

Examination of the data in Table 4 permits several generalizations:

1. The reaction is catalytic and proceeds by stepwise nucleophilic attack and subsequent regeneration of the nucleophile.

$$R_3SiCB_{10}H_{10}CSiR_3 + F^- \rightleftarrows R_3SiCB_{10}H_{10}C^- + R_3SiF$$

$$R_3SiCB_{10}H_{10}C^- + H_2O \rightarrow R_3SiCB_{10}H_{10}CH + {}^-OH$$

$$R_3SiF + {}^-OH \rightarrow R_3SiOH + F^-$$

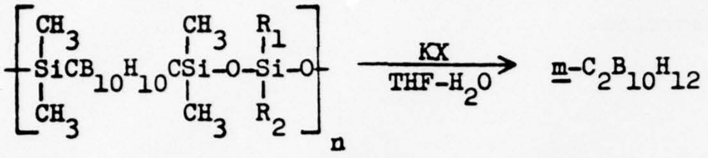
2. A phase transfer catalyst increases the rate of reaction, but is not essential in many cases.
3. F^- and ^-OH are satisfactory nucleophiles; however, F^- is preferred because of its greater selectivity.
4. The technique is applicable to ortho, meta, and para derivatives.
5. Cured and compounded materials are reactive. Apparently, even though the cross-linked polymers are essentially insoluble, solvent swelling provides sufficient contact for the reaction to take place.
6. Carborane cage cleavage is not observed. Treatment of the aqueous layers with Me_4NCl did not give $Me_4NC_2B_9H_{12}$.

2.3.2 Recycling of UCARSIL Polymers

A selective method for the cleavage of silylated carboranes has been established. Recycling of carborane containing by-products should ultimately permit the quantitative conversion of o-carborane to m-disilanol in the three-step preparative sequence. This has been confirmed experimentally.

TABLE 4

CLEAVAGE OF SILYLATED CARBORANES

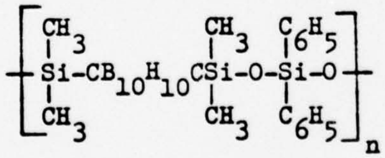


$$\left[-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{Si}}CB_{10}H_{10}C\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{Si}}-O-\overset{\overset{\textstyle R_1}{|}}{\underset{\underset{\textstyle R_2}{|}}{Si}}-O-\right]_n \xrightarrow[THF-H_2O]{KX} \underline{m}-C_2B_{10}H_{12}$$

Carborane	KX (wt % of carborane)	Catalyst	Yield (%)
UCARSIL	KF (33)	Adogen 464	91
Dexsil 202[a]	KF (50)	none	93
Dexsil 202	KF (10)	Adogen 464	94
Dexsil 202	KOH (10)	Adogen 464	93
Dexsil 202	KOH (10)	none	93
$\underline{o}$-$C_2B_{10}H_{10}(SiMe_2Cl)_2$	KF (10)	Adogen 464	91
$\underline{p}$-$C_2B_{10}H_{10}(SiMe_2OH)_2$	KF (10)	Adogen 464	95

- -

a) Dexsil 202 is:



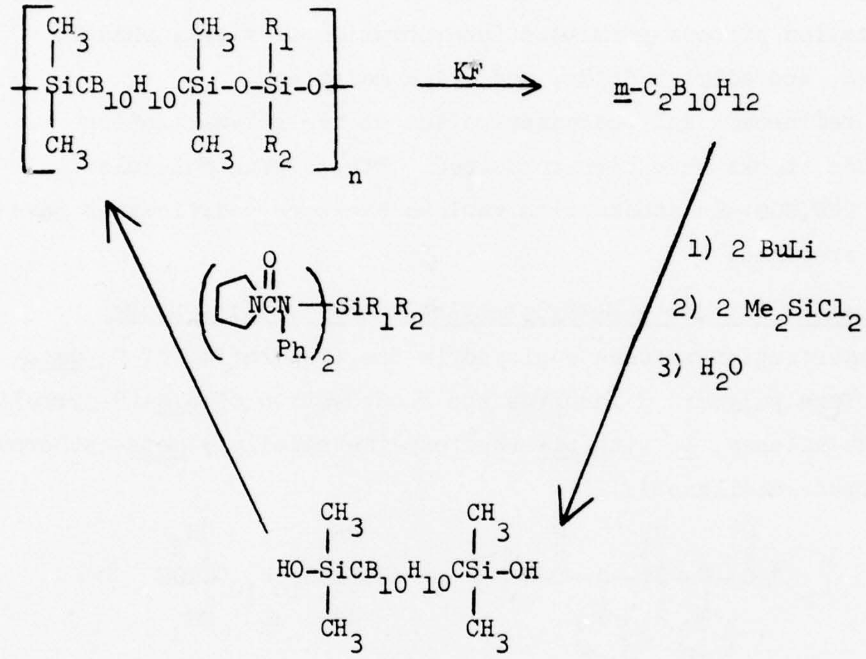
$$\left[-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{Si}}-CB_{10}H_{10}C\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{Si}}-O-\overset{\overset{\textstyle C_6H_5}{|}}{\underset{\underset{\textstyle C_6H_5}{|}}{Si}}-O-\right]_n$$

and contains 30% carborane by weight.

Thus, >95% of the carborane moiety can be accounted for either as m-$C_2B_{10}H_{10}(SiMe_2OH)_2$ or as recovered carborane (Figure 4). This amounts to a 30-35% increase in efficiency. In addition, carborane-siloxane polymers with marginal performance characteristics can be returned to m-carborane and recycled.

FIGURE 4

RECYCLING OF SILYLATED CARBORANES



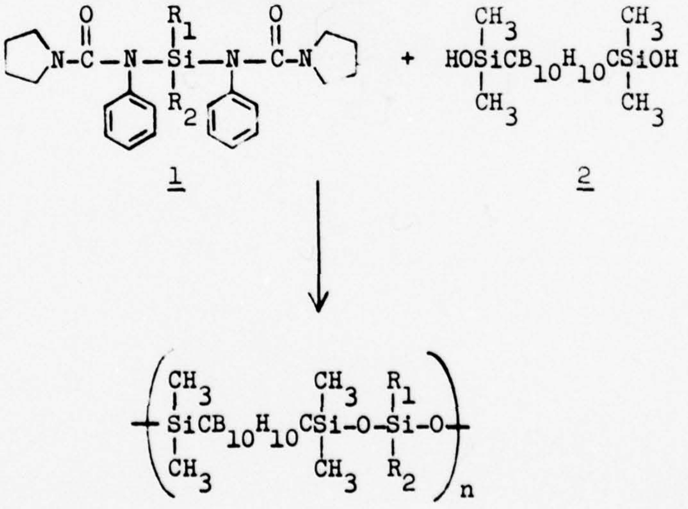
3.0 PREPARATION AND CHARACTERIZATION OF UCARSIL STOCKS

The bis-ureidosilane carboranedisilanol polymerization process was developed at Union Carbide in 1971-1973.[7] Prior synthetic problems relating to the preparation of D_2-carborane-siloxane were circumvented and high molecular weight ($\bar{M}_w = 150{,}000$), linear stocks were prepared. Moreover, this polymerization process permitted incorporation of vinyl, phenyl, trifluoropropyl, and silyl hydride, modifying moieties.

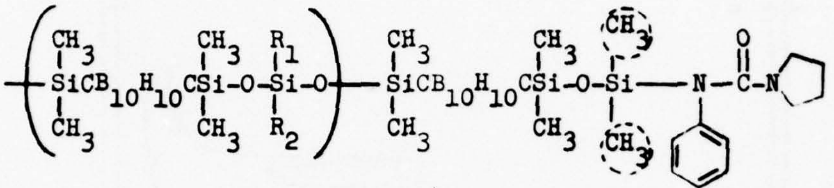
Further refinement and characterization of the polymerization reaction and the stocks have been conducted. Stocks with molecular weights up to 280,000 and stocks with various backbone modification have recently been prepared.

3.1 Polymerization Studies - Methylphenylsiloxane Modified Stock

The polymerization process employed in the preparation of D_2-meta-carborane-siloxane polymers 3 involves the condensation of bis-(N-pyrrolidino-N'-phenylureido)silanes, 1, with bis-(hydroxydimethylsilyl)-meta-carborane, 2 (i.e., carborane disilanol).



Nuclear magnetic resonance (100 MHz nmr) spectroscopy is used to monitor the reaction stoichiometry, adjusting for side reactions and monomer impurities. This nmr technique has been documented for the preparation of D_2-carborane-dimethylsiloxane and D_2-carborane-dimethyl/diphenylsiloxane (67/33 mole %) polymers. Using 100 MHz nmr, one can differentiate between the silane methyl groups on the polymer (3; $R_1=R_2=CH_3$), bis-(N-pyrrolidino-N'-phenylureido)dimethylsilane (1; $R_1=R_2=CH_3$), and dimethylsilylurea end groups on the polymer, 4.

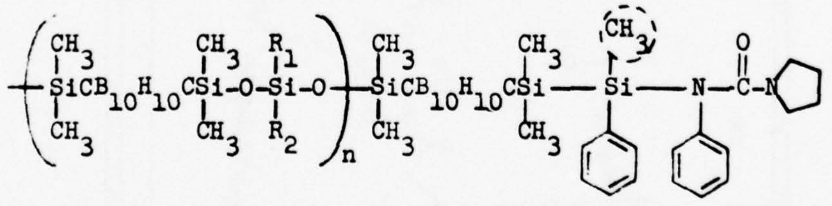


4

This is exemplified in Figure 5.

In order to obtain better low temperature properties, 33 mole % methylphenylsiloxane was incorporated into the D_2-carborane-dimethylsiloxane polymer. Thus, the preferred polymer now contains methylphenylsiloxane moieties. These methyl groups complicate the spectrum as shown in Figure 6. For this reason, peak assignments are made according to downfield shifts caused by the phenylsilanes and are shown in Figure 7.

During the polymerization reaction, one can observe dimethylsilylurea end groups, 4, and methylphenylsilylurea end groups, 5.



5

This is exemplified in Figures 8 and 9. Fortunately, the dimethylsilylurea end group appears slightly upfield from the methylphenylsiloxanes in the polymer.

The nmr technique can be used to adjust the stoichiometry of methylphenylsiloxane modified polymer. After the initial addition of carborane disilanol to the reaction, end groups are analyzed by nmr. Since twice as much dimethyl-bis-urea is used in the reaction, the dimethylsilylurea end groups should predominate. If the nmr shows no end groups, then the polymer chains are terminated with carborane silanols, 6.

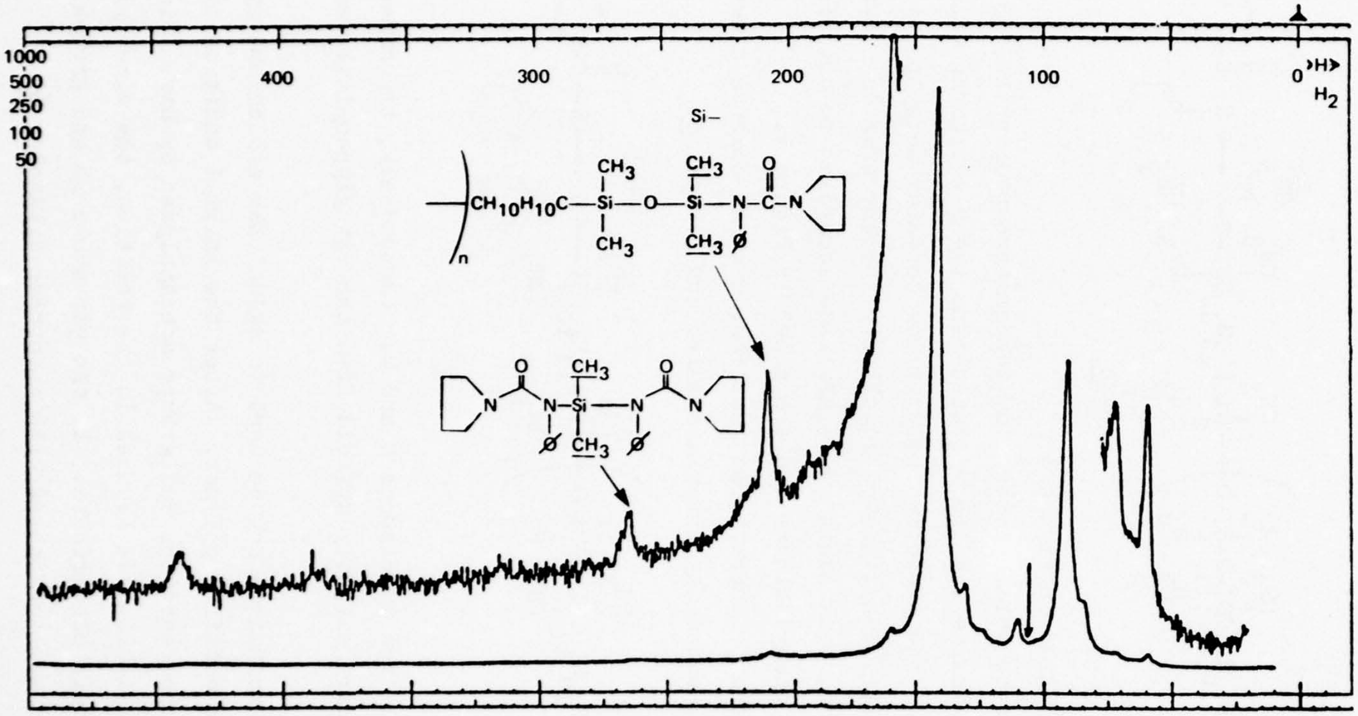


FIGURE 5. D_2-CARBORANE-DIMETHYLSILOXANE REACTION MIXTURE

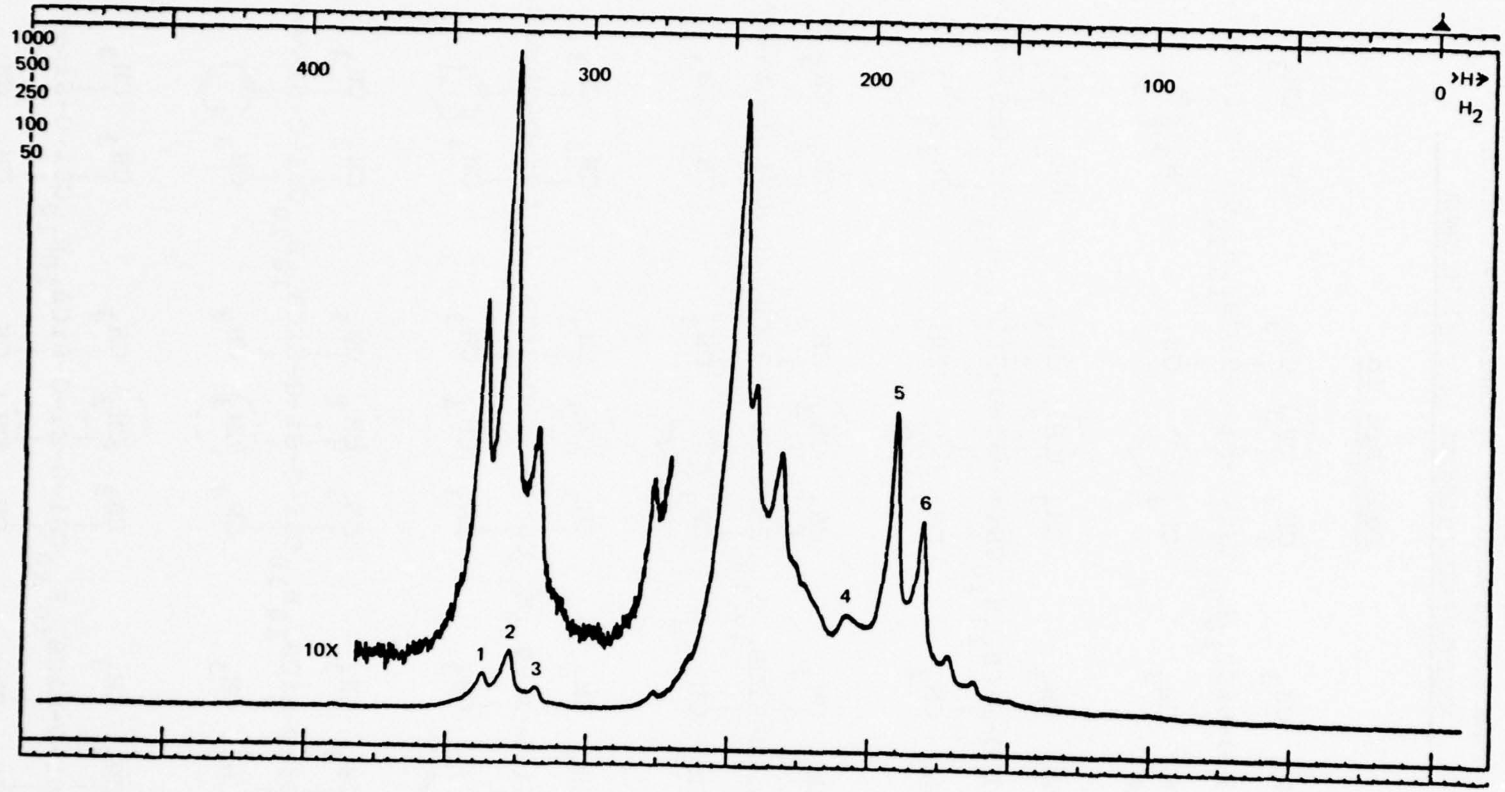
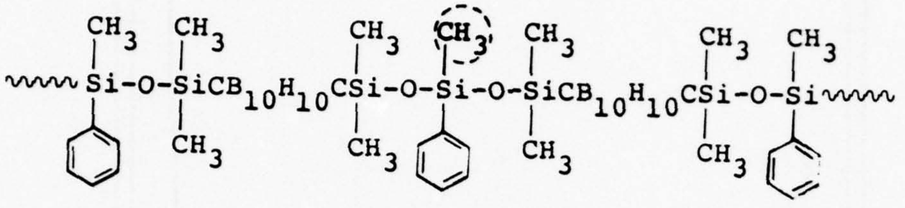


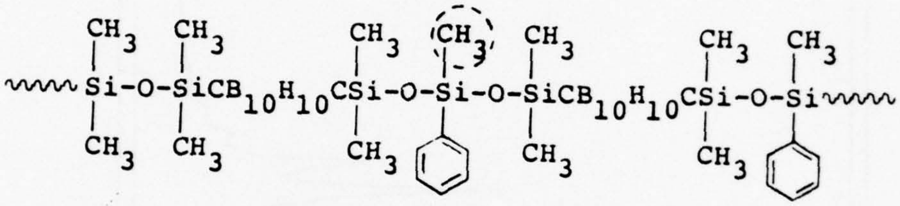
FIGURE 6. D_2-CARBORANE-DIMETHYL/METHYLPHENYLSILOXANE (67/33) POLYMER

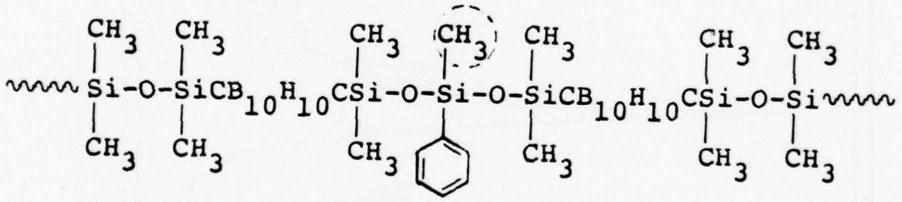
FIGURE 7

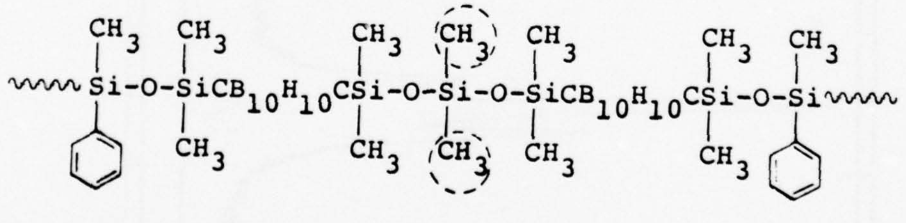
PEAK ASSIGNMENTS FOR D_2-CARBORANE-DIMETHYL/METHYLPHENYLSILOXANE (67/33) POLYMER

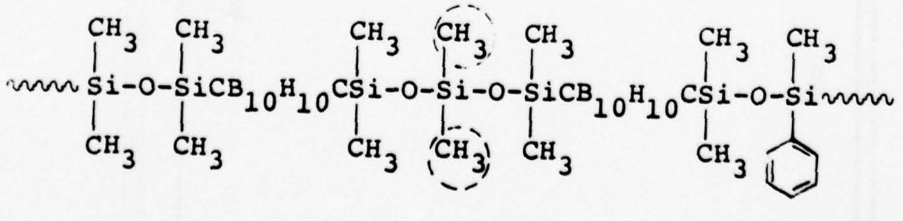
Peak No. **Peak Due To**

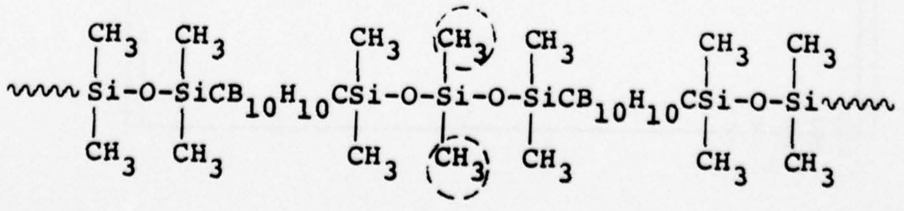
1


2


3


4


5


6


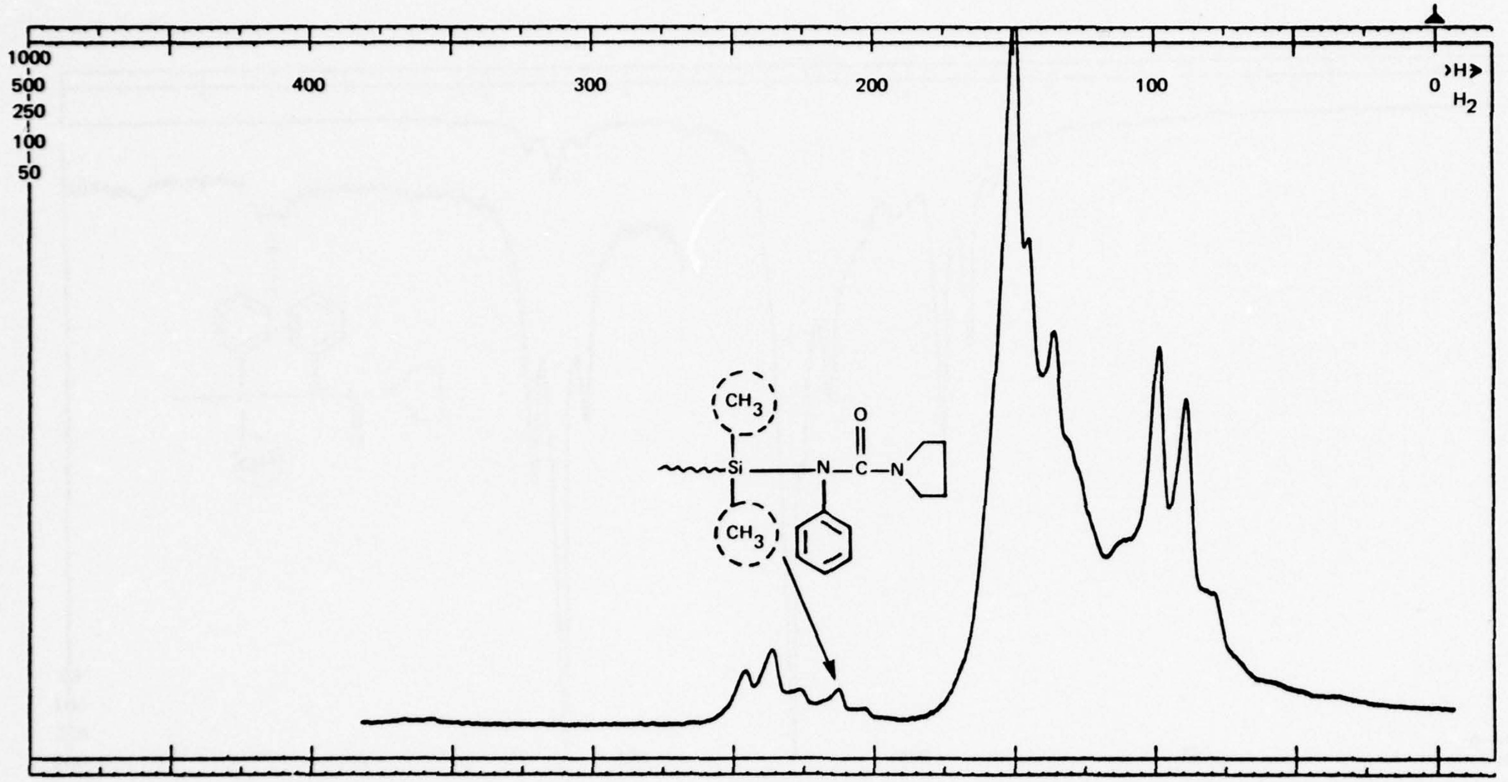


FIGURE 8. DIMETHYLSILYLUREA END GROUP IN D_2-CARBORANE-DIMETHYL/METHYLPHENYLSILOXANE (67/33) POLYMER

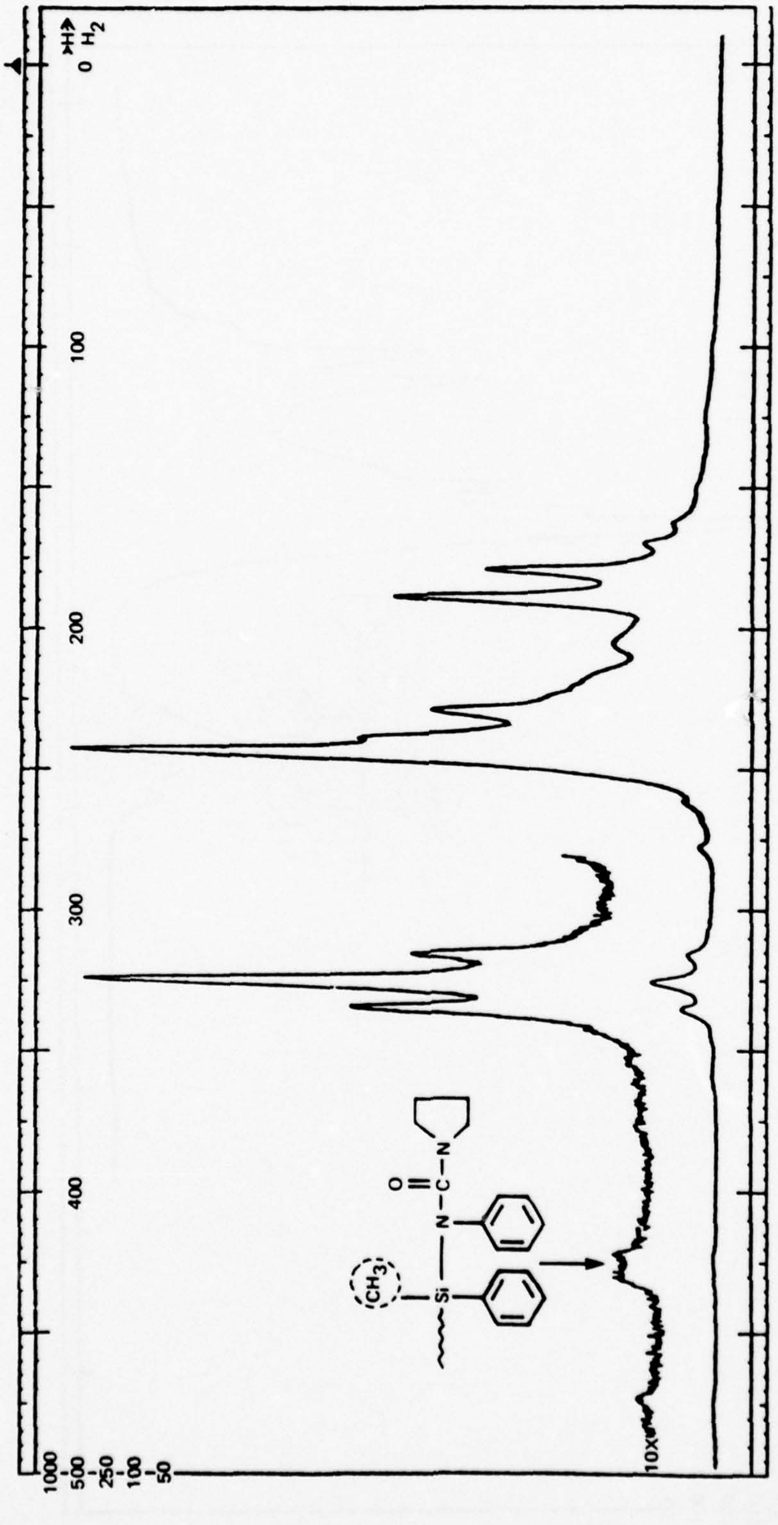
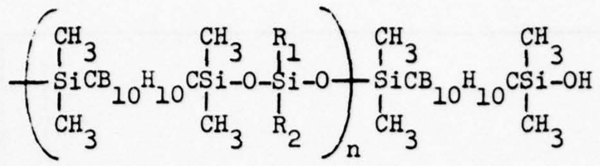


FIGURE 9. METHYLPHENYLSILYLUREA END GROUP IN D_2-CARBORANE-DIMETHYL/METHYLPHENYLSILOXANE (67/33) POLYMER



$$-\!\left(\mathrm{Si(CH_3)_2CB_{10}H_{10}CSi(CH_3)_2\text{-}O\text{-}SiR_1R_2\text{-}O}\right)_n\!-\mathrm{Si(CH_3)_2CB_{10}H_{10}CSi(CH_3)_2\text{-}OH}$$

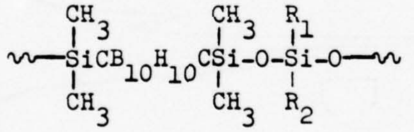
6

To further increase the molecular weight, bis-(N-pyrrolidino-N'-phenylureido)methylphenylsilane (1; R_1=CH_3, R_2=phenyl) is added.

The nmr spectra of the polymer with methylphenylsilane monomer (1; R_1=CH_3, R_2=phenyl) is shown in Figure 10.

3.2 Thermal Properties of UCARSIL Stocks

D_2-carborane-dimethylsiloxane, diphenylsiloxane, methylphenylsiloxane and dimethyl/methylphenylsiloxane (67/33 and 33/67 mole %) modified 7 a-e stocks were prepared and characterized by differential scanning calorimetry (DSC) and thermogravimetry. The weight average molecular weight, $\bar{M}_w$, was 20-50,000 for most of these stocks. Only one of the stocks contained any vinyl groups.



$$\sim\mathrm{Si(CH_3)_2CB_{10}H_{10}CSi(CH_3)_2\text{-}O\text{-}SiR_1R_2\text{-}O}\sim$$

7

a - R_1, R_2 = CH_3
b - R_1, R_2 = phenyl
c - R_1 = CH_3; R_2 = phenyl
d - R_1, R_2 = CH_3/R_1 = CH_3; R_2 = phenyl (67/33 mole %)
e - R_1, R_2 = CH_3/R_1 = CH_3; R_2 = phenyl (33/67 mole %)

The DSC glass transition temperatures (Tg) are listed in Table 5. As reported earlier, the D_2-carborane-dimethylsiloxane was crystalline and showed a double melting endotherm with peaks at 79 and 93°C. Diphenylsiloxane and methylphenylsiloxane moieties are used to suppress the crystallization of D_2-carborane-dimethylsiloxane; however, the Tg increases simultaneously with depression of melting. Figure 11 shows the relationship between the glass transition temperatures and the mole percent of either

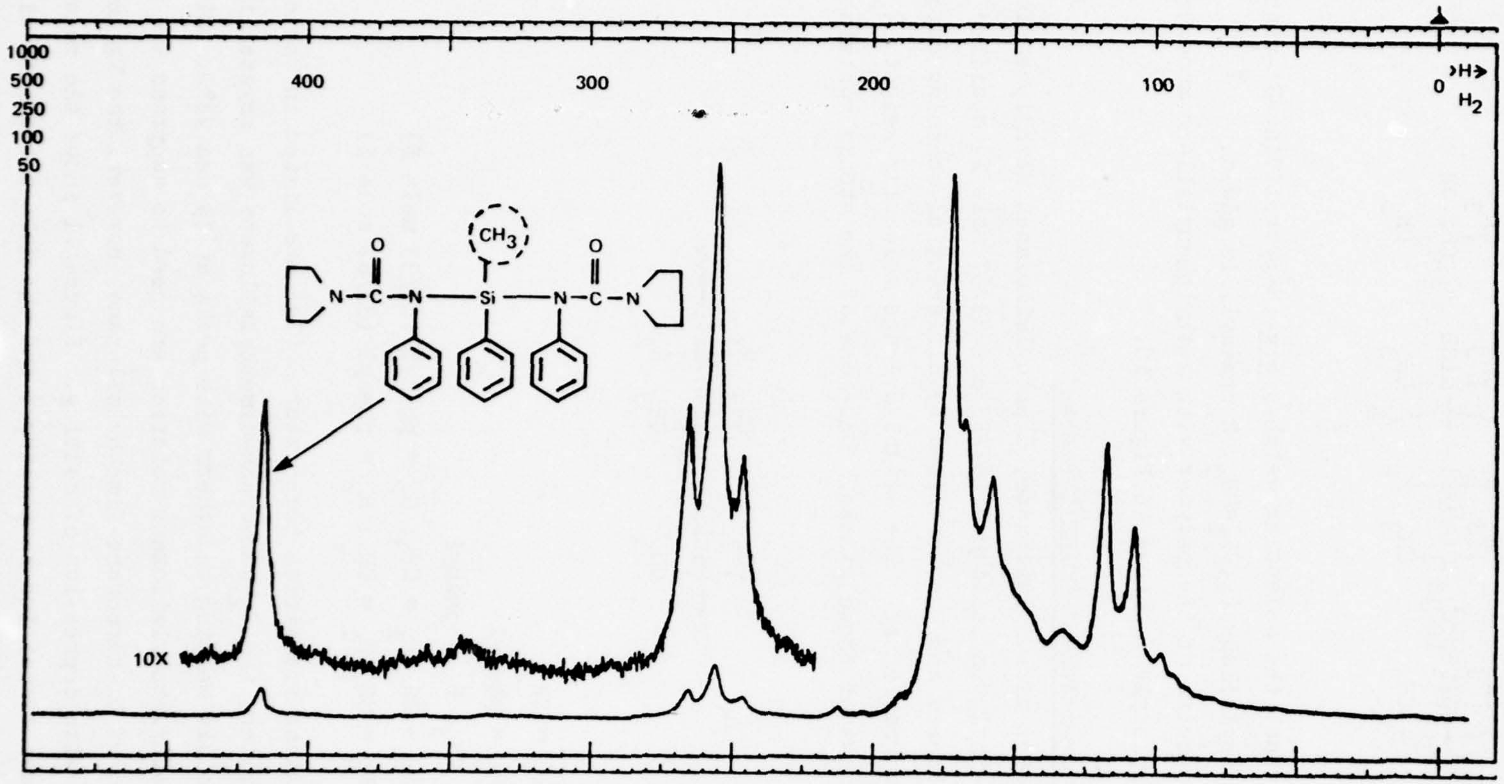


FIGURE 10. D_2-CARBORANE-DIMETHYL/METHYLPHENYLSILOXANE (67/33) POLYMER WITH METHYLPHENYLSILANE-BIS-UREA MONOMER

TABLE 5

GLASS TRANSITION TEMPERATURE OF D_2-CARBORANE-SILOXANE STOCK*

Sample	Composition	$\bar{M}_w$	Tg,°C
10352-61	D_2-carborane-dimethylsiloxane	40,000	-50**
10352-97	D_2-carborane-dimethyl/methylphenylsiloxane (67/33 mole %)	50,000	-36
10352-110-2	D_2-carborane-dimethyl/methylphenylsiloxane (33/67 mole %)	120,000	-22
10352-101	D_2-carborane-methylphenylsiloxane	30,000	-14
10352-115-3	D_2-carborane-diphenylsiloxane	20,000	+20
10192-122	D_2-carborane-dimethyl/diphenylsiloxane (33/67 mole %)***	157,000	-24

* Perkin-Elmer DSC-2, 10°C/min heating and cooling rate.

** Very weak.

*** Also contains 4 mole % methylvinylsiloxane.

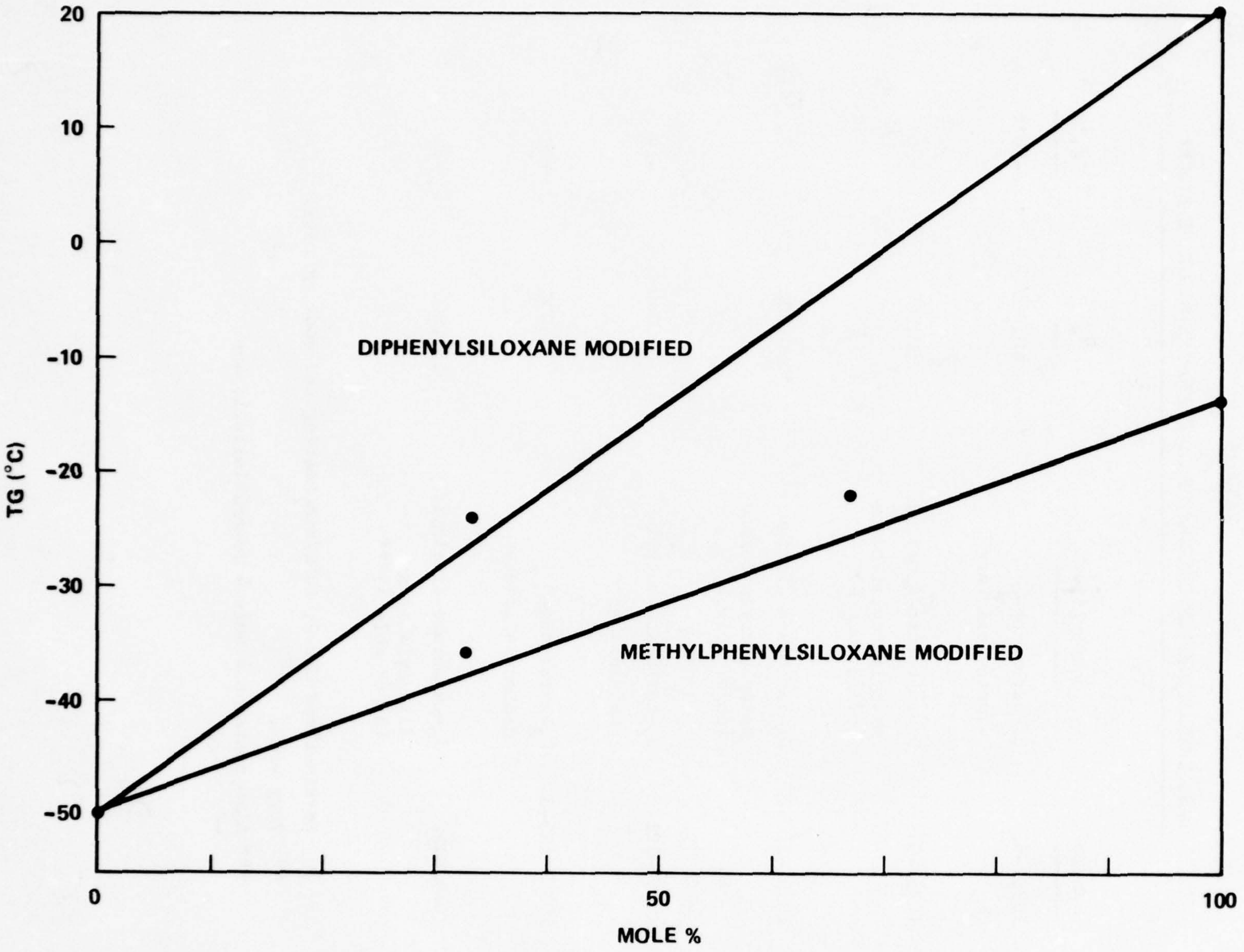


FIGURE 11. TG vs. COMPOSITION OF D_2-CARBORANE-SILOXANES

diphenylsiloxane or methylphenylsiloxane. The Tg of the modified stock should be as low as possible to have good low temperature properties; therefore, the low Tg profile of the methylphenylsiloxane modified material makes it preferred over the diphenylsiloxane modification.

Figures 12-16 show the thermal oxidative characteristics of the stocks as characterized by thermogravimetry. Among the stocks, D_2-carborane-methylphenylsiloxane appeared to be the most stable, exhibiting the lowest weight loss at elevated temperatures.

Modification with 33 mole % methylphenylsiloxane greatly improves the thermal stability of D_2-carborane-dimethylsiloxane. This observation is corroborated by recent unpublished results from J. K. Gillham (Princeton University) who studied isothermal oxidation at 325°C by torsional braid analysis (TBA). The 33 mole % methylphenylsiloxane modified stock showed significantly improved oxidation resistance relative to D_2-carborane-dimethylsiloxane, as evidenced by modulus/time performance characteristics (i.e., rate of modulus increase resulting from cross-linking reactions).

3.3 Mechanical Properties of Stocks as a Function of Molecular Weight

The mechanical properties were determined for methylphenylsiloxane modified (33 mole %) D_2-carborane-dimethylsiloxane stocks with molecular weights ranging from 60,000 to 249,000, and for 33 mole % diphenylsiloxane modified stock with molecular weights of 150,000 and 283,000. The results are summarized in Tables 6 and 7. Clearly, a "quantum jump" in elongation was achieved through increasing the molecular weight of the stock from 150,000 to 249,000 and 283,000.

3.4 Polymerization Studies - Bis-Sulfonamide Silane Monomer

In our search for new, less expensive, and more convenient methods of preparing carborane-siloxane polymers, it was decided to investigate silane monomers with sulfonamide leaving groups. Thus, bis-sulfonamidodimethylsilane, 8, was reacted with carborane disilanol in chlorobenzene, this process should yield D_2-carborane-dimethylsiloxane, 9, and N-methyl-p-toluene-sulfonamide, 10. The reaction was quite slow at room temperature; therefore, the reaction was heated to 100-105°C and monitored by nmr

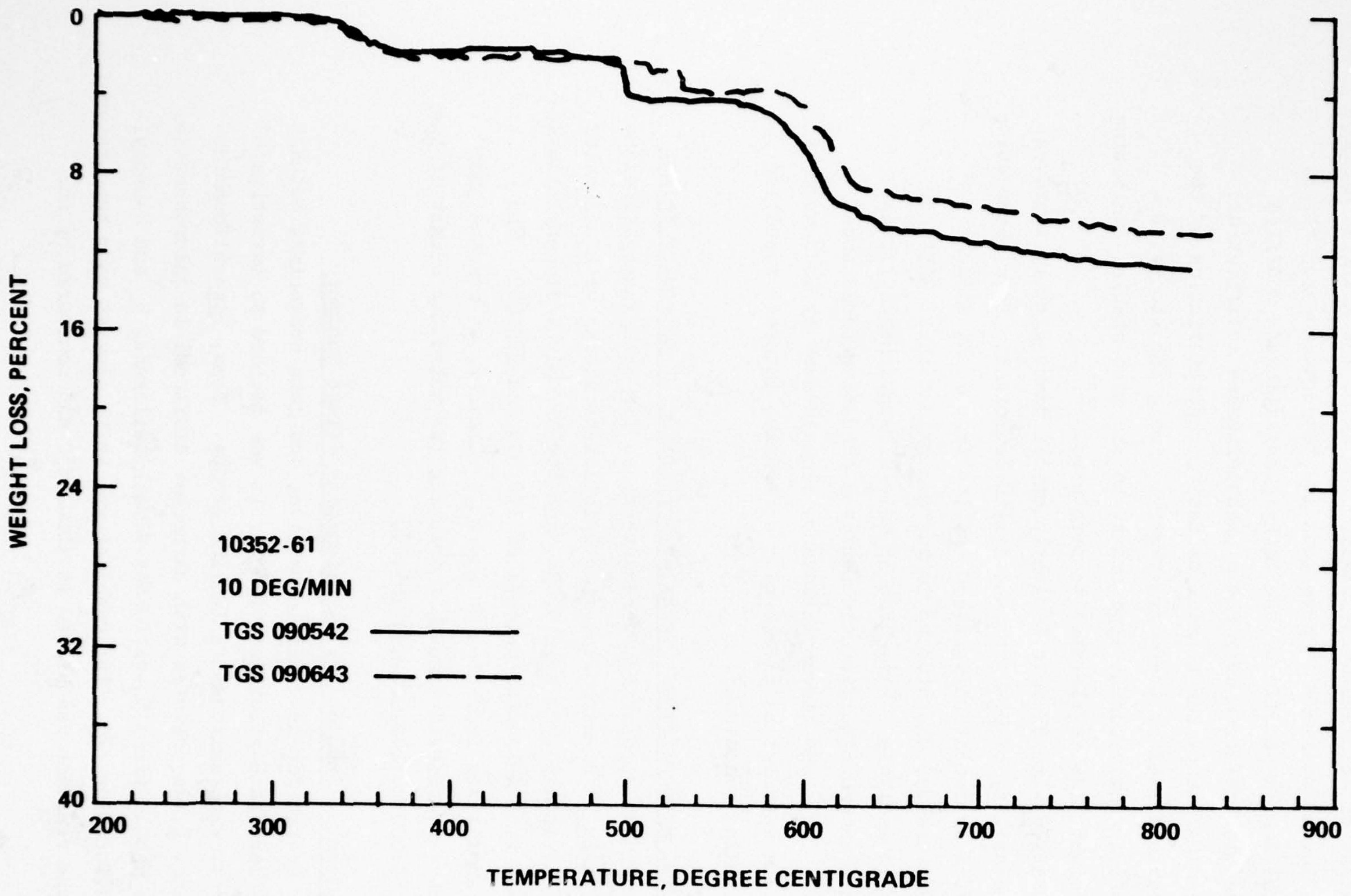


FIGURE 12. THERMOGRAVIMETRY OF D_2-CARBORANE-DIMETHYLSILOXANE IN AIR

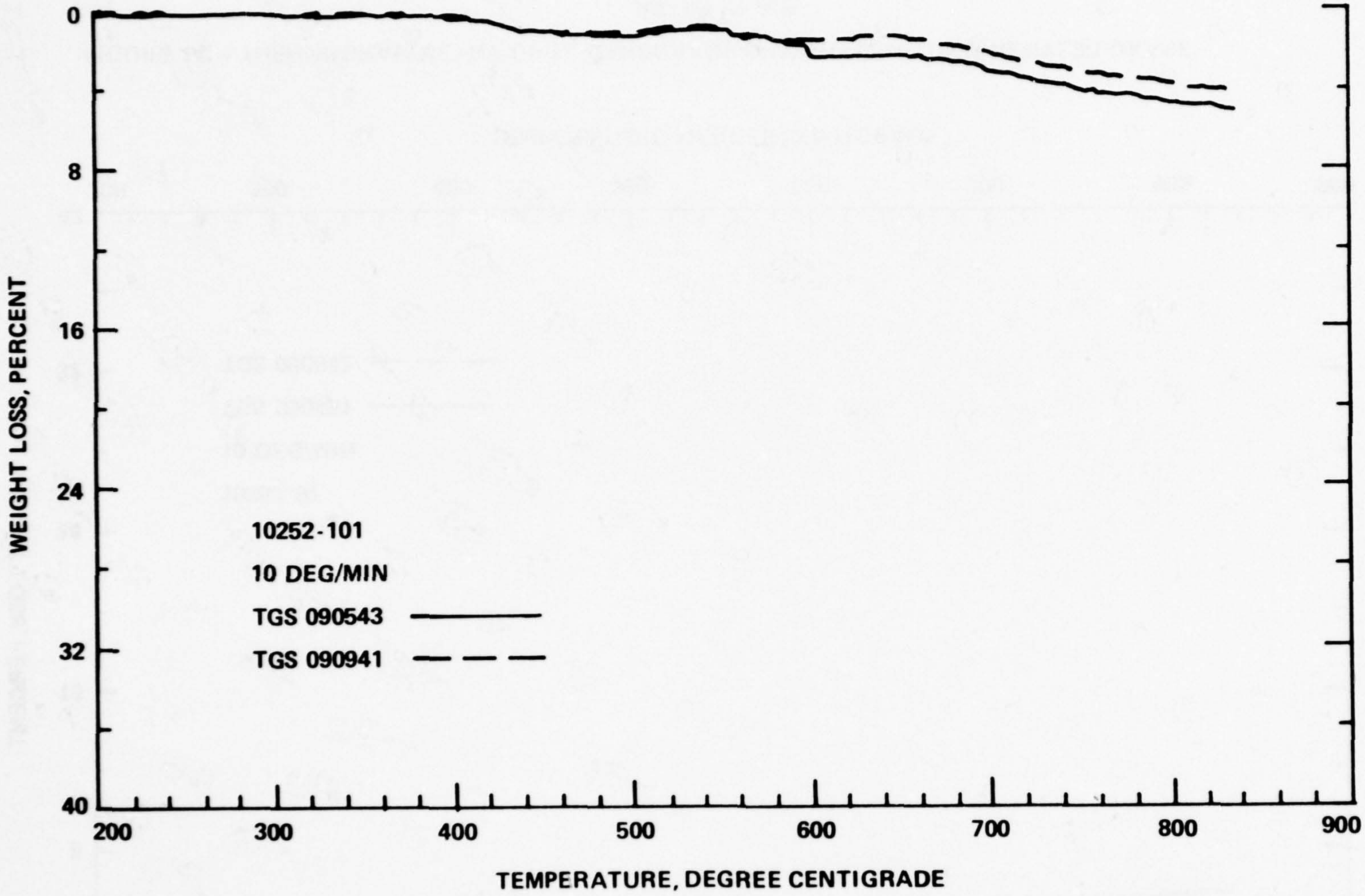


FIGURE 13. THERMOGRAVIMETRY OF D_2-CARBORANE-METHYLPHENYLSILOXANE IN AIR

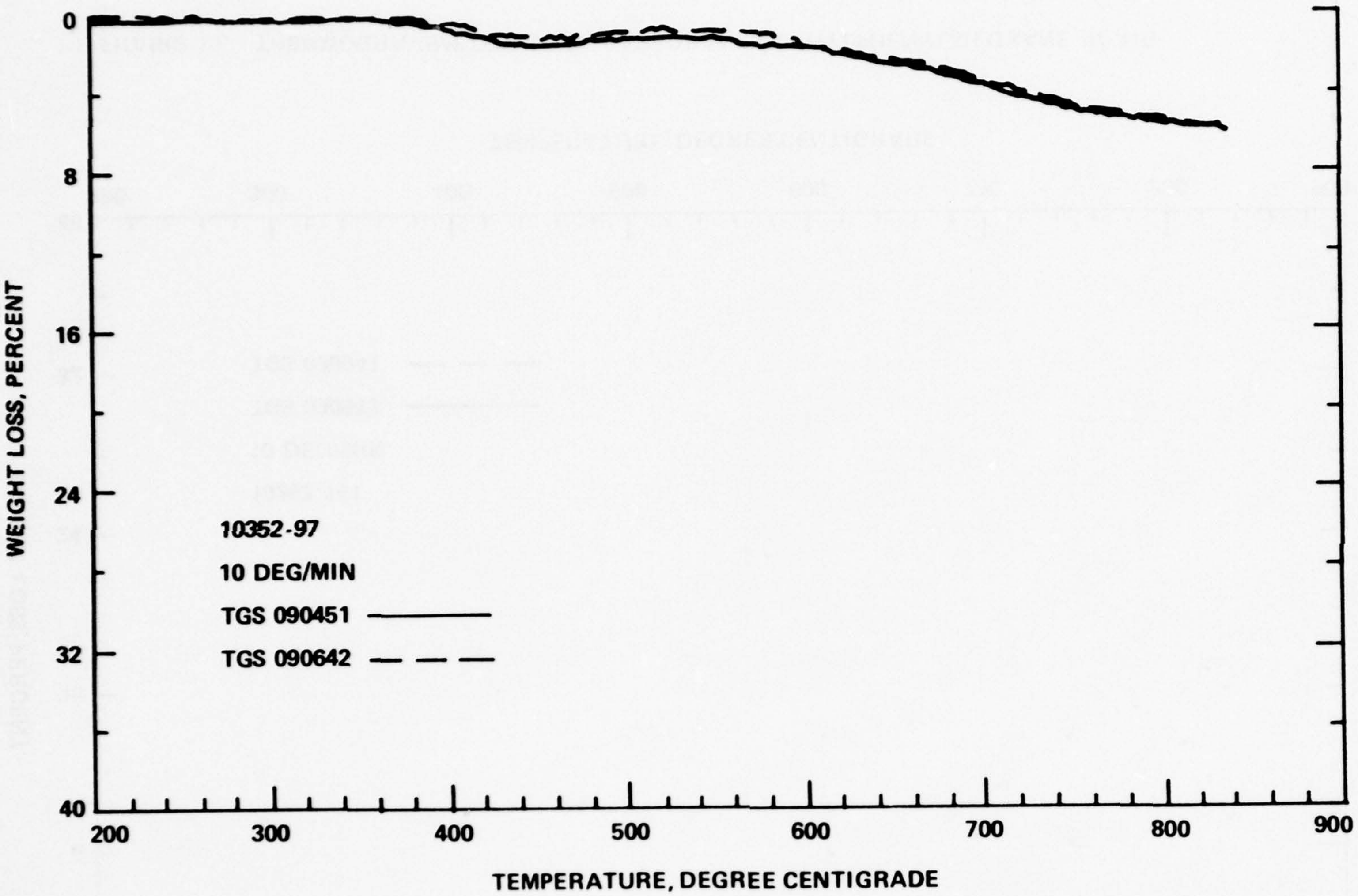


FIGURE 14. THERMOGRAVIMETRY OF D_2-CARBORANE-DIMETHYL/METHYLPHENYLSILOXANE (67/33) IN AIR

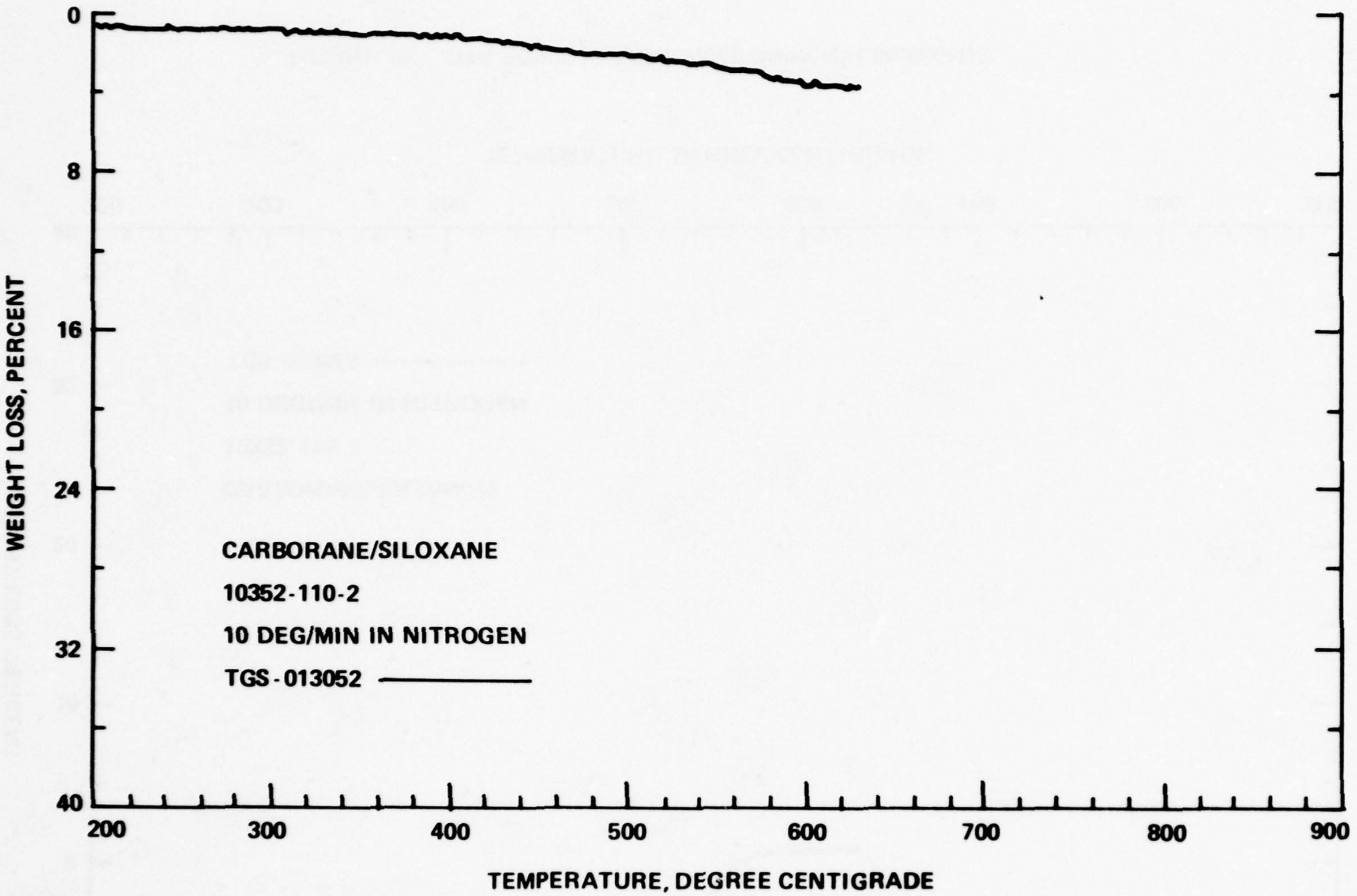


FIGURE 15. TGA FOR D_2-CARBORANE-DIMETHYL/METHYLPHENYLSILOXANE (33/67)

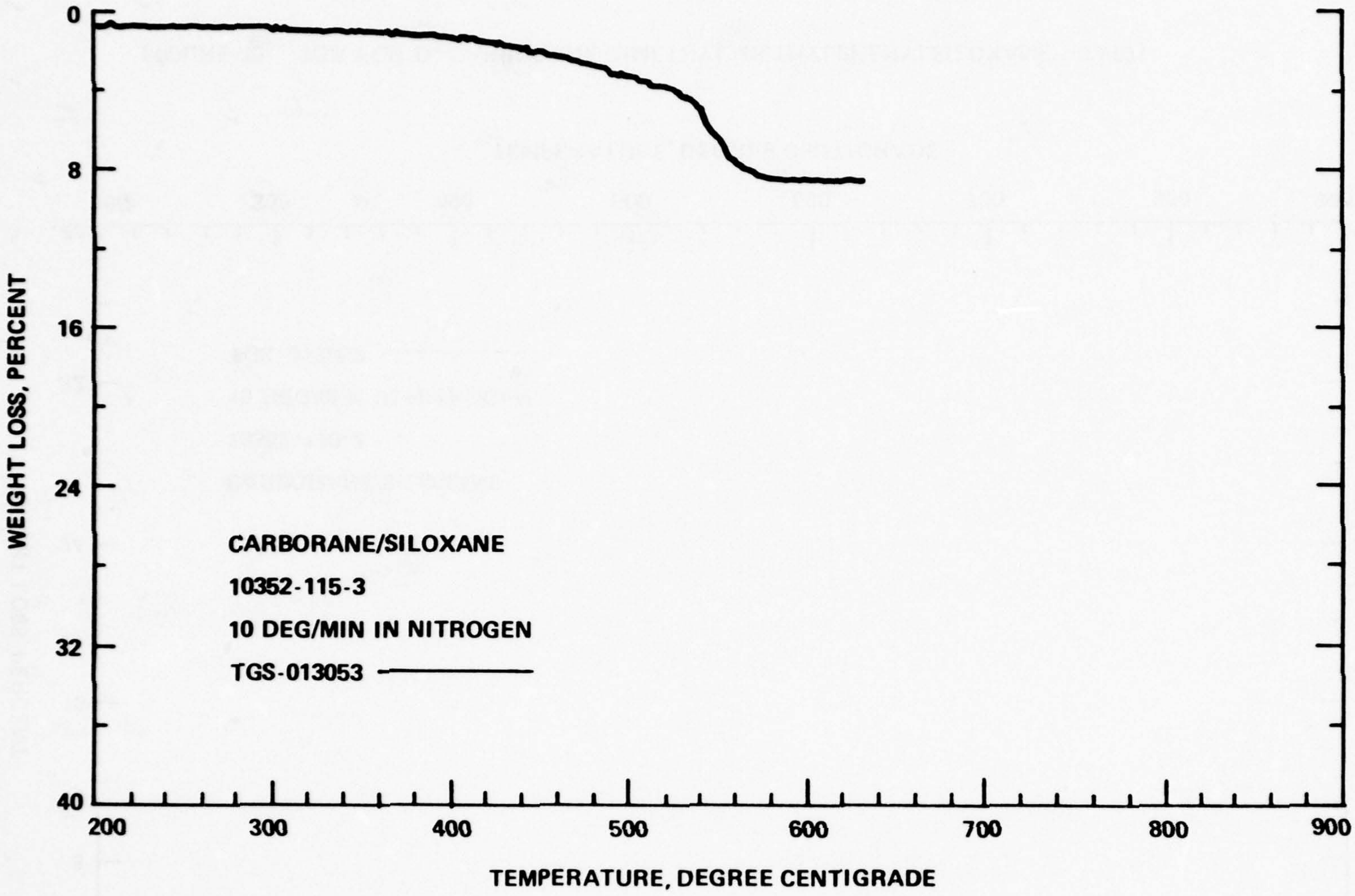


FIGURE 16. TGA FOR D_2-CARBORANE-DIPHENYLSILOXANE

TABLE 6

MECHANICAL PROPERTIES OF METHYLPHENYL MODIFIED STOCKS AS A FUNCTION OF MOLECULAR WEIGHT*

$\bar{M}_w$	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %
60,000	6400	160	6
150,000	5800	220	14
249,000	4000	250	550

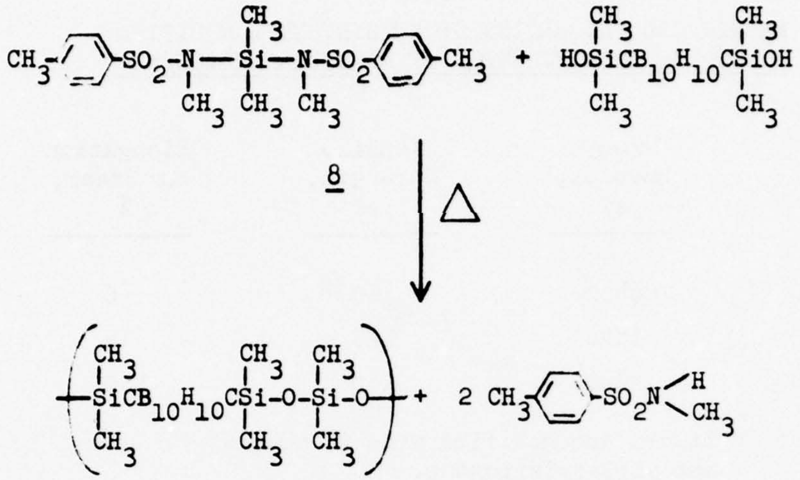
* Stocks are modified with 33 mole % methylphenylsiloxane.

TABLE 7

MECHANICAL PROPERTIES OF DIPHENYL MODIFIED STOCKS AS A FUNCTION OF MOLECULAR WEIGHT*

$\bar{M}_w$	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %
150,000	2900	103	60
283,000	3300	333	700

* Stocks are modified with 33 mole % diphenylsiloxane.

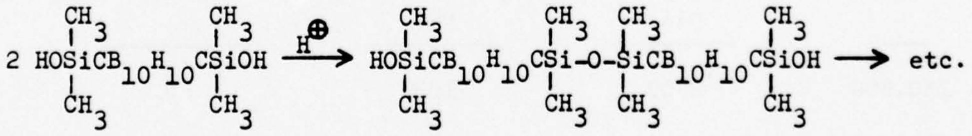


8

9

10

spectroscopy. After 3 hours, the amount of carborane disilanol had decreased significantly compared to the bis-sulfonamide. This is not what one would expect if polymer (9) is being formed. After 20 hours, almost all the carborane disilanol reacted; however, most of the bis-sulfonamide still remained unreacted. These observations suggest that the carborane disilanol is reacting but not with the bis-sulfonamide. It is known that carborane disilanol will self-condense under acidic conditions and it is probable that this side reaction is occurring:



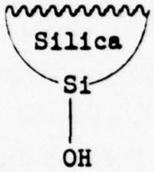
$$2\ HO\underset{CH_3}{\overset{CH_3}{Si}}CB_{10}H_{10}C\underset{CH_3}{\overset{CH_3}{Si}}OH \xrightarrow{H^{\oplus}} HO\underset{CH_3}{\overset{CH_3}{Si}}CB_{10}H_{10}C\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}CB_{10}H_{10}C\underset{CH_3}{\overset{CH_3}{Si}}OH \longrightarrow \text{etc.}$$

Any N-methyl-p-toluenesulfonamide formed in the initial stages of the reaction is probably acidic enough to cause carborane disilanol self-condensation.

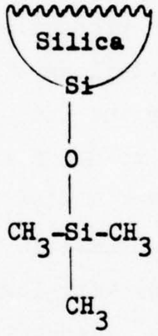
The results indicate that only highly reactive silyl derivatives can be utilized for D_2-carborane-siloxane polymer formation. This conclusion is substantiated by early results with other moderately reactive dimethylsilyl derivatives.

4.0 PROPERTIES OF COMPOUNDED AND CURED STOCKS

A necessary understanding of filler-resin interactions was achieved in 1973-1974.[1,8] As a result, significant improvements in the retention of mechanical properties after heat aging in air at 315°C for 300 hours was obtained by using reinforcing silicas with nonacidic surfaces. Reactions between surface silanols on regular silica fillers and phenylsiloxane moieties in the polymer were circumvented. The preferred filler for long term retention of properties was Silanox 101.



fumed silica
Cab-O-Sil



hydrophobic silica
Silanox 101

From this study our attention focused on extending fillers, optimizing peroxide and ferric oxide concentrations, solvent resistance, and property losses during heat aging. A better understanding of the compounding and curing variables has accordingly been achieved. The latter study has also indicated a method for improved solvent resistance.

Utilizing data from the optimization studies conducted in the past two years, we have achieved marked improvements in performance through formulation and vulcanization changes. Further, a fundamental basis has been established for predicting and interpreting formulation and fabrication variables. Our significant background gained in these studies has facilitated application development activities.

4.1 D_2-Carborane-Dimethyl/methylphenylsiloxane Vulcanizates

In previous studies the 33 mole % methylphenylsiloxane modified carborane-dimethylsiloxane stock was characterized as an amorphous material with a Tg at -37°C; this modification afforded a non-crystalline system with ~13°C lower Tg than the diphenylsiloxane modified stocks.[1,17] Henceforth, methylphenylsiloxane modified stock has been used in various formulation studies to evaluate compounding and curing variables. Described below are formulation studies utilizing this preferred stock.

4.1.1 Mechanical Properties as a Function of Temperature

The mechanical properties of a compounded and cured D_2-carborane-dimethyl/methylphenylsiloxane (66/33 mole %) stock with 30 phr Silanox 101, 2.5 phr ferric oxide and 2.5 phr dicumyl peroxide ($\bar{M}_w$ 250,000) was determined from -40 to 300°C and are listed in Table 8. The modulus remained constant over a wide range: -10 to 300°C. The tensile strength decreased with an increase in temperature. The elongation at break decreased at high and very low temperatures. The difference between this and a previous study[8] [stock 10352-27 ($\bar{M}_w$ 100,000; 33 mole % methylphenyl modified) with 20 phr Cab-O-Sil, 1 phr ferric oxide and 2 phr benzoyl peroxide] are the better low temperature properties between -20 and -40°C for the recent system.

The tensile strengths and elongations for both systems at low temperatures are compared in Table 9, providing an indication of the effect of molecular weight on properties.

4.1.2 Temperature-Retraction Test

A temperature-retraction procedure was used to assess the low temperature performance (ASTM D 1329-72) of a compounded and cured methylphenylsiloxane (33 mole %) modified stock with 30 phr Silanox 101, 2.5 phr ferric oxide and 2.5 phr dicumyl peroxide. This test is useful for the selection of materials for low-temperature service. Thus, an elastomer is stretched to 3/4 of its ultimate elongation, frozen, allowed to warm at a rate of 1°C/minute and the temperatures at which 10 percent (TR10) and 70 percent (TR70) retraction occurs are recorded.

TABLE 8

MECHANICAL PROPERTIES AS A FUNCTION OF TEMPERATURE*

Temp., °C	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %
300	500	59	15
260	540	116	30
200	576	157	40
25	500	519	130
-20	2,500	558	180
-30	30,800	1,510	55
-40	140,300	2,100	20

* Stock 10352-78 (33 mole % methylphenylsiloxane) with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

- -

TABLE 9

COMPARISON OF MECHANICAL PROPERTIES AS A FUNCTION OF TEMPERATURE, MOLECULAR WEIGHT AND PEROXIDE

	Present Results*		Former Results**	
Temp., °C	Tensile Strength, psi	Elongation at Break, %	Tensile Strength, psi	Elongation at Break %
25	519	130	505	220
-20	558	180	420	90
-30	1,510	55	530	20
-40	2,100	20	1,100	5

* Stock 10352-78 ($\bar{M}_w$ 250,000; 33 mole % methylphenyl) with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

**Stock 10352-27 ($\bar{M}_w$ 100,000; 33 mole % methylphenyl) with 20 phr Cab-O-Sil, 1 phr ferric oxide and 2.0 phr benzoyl peroxide.

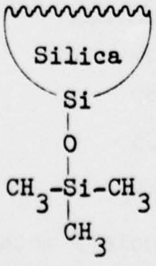
TR10 and TR70 values of -38 and -24°C, respectively, were obtained. TR70 correlates with low temperature compression set and TR10 has been found to correlate with brittle points in vulcanizates.

4.1.3 Solvent Resistance

The resistance to various solvents is a critical characteristic of high performance elastomers. A previous study[8] was conducted using a base stock with a low molecular weight gel permeation chromatograph tail ($\bar{M}_w = 112{,}000$); this low molecular weight tail was thought to be extractable and thereby reduce the solvent resistance. In the present study a compound and cured stock with no low molecular weight tail ($\bar{M}_w = 250{,}000$) was employed. Following ASTM test method D471-72 (immersion for seven days at ambient temperatures), the mechanical properties before and after testing were demonstrated to remain constant; results are summarized in Table 10. A comparison of the percent swell of high temperature elastomers are shown in Table 11. Our D_2-carborane-siloxane overall appears better than the other high temperature elastomers with the exception of Viton B (except in acetone). However, to qualify for many advance system applications (aircraft and electronic), additional improvements in solvent resistance will be necessary. A subsequent section on trifluoropropyl modified carborane-siloxane elastomers addresses this factor in additional detail.

4.1.4 Extending Fillers

In previous studies, Silanox 101, a hydrophobic silica, was shown to be the best reinforcing filler on the basis of good retention of mechanical properties after heat aging in air at 315°C.[8]



Silanox 101

TABLE 10

SOLVENT RESISTANCE - MECHANICAL PROPERTIES*

Solvent**	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %	% Swell
None	500	519	130	--
H_2O	533	573	110	0.46
Ethanol	496	556	115	2.23
Methanol	453	565	110	1.67
Toluene	457	553	110	162
Acetone	487	501	100	48.6
Xylene	533	491	100	151
CCl_4	507	645	125	146
Reference Fuel B	431	645	125	113

* Stock 10352-78 with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

** ASTM test method D-471-72 immersed seven days at room temperature.

TABLE 11

SOLVENT RESISTANCE OF HIGH TEMPERATURE ELASTOMERS*

Solvent	% Swell[1] UCARSIL[2]	SE-7501U[3]	Silastic 52U[4]	Dexsil 300/400[5]	Viton B[6]
Acetone	48.6	30.8	31.1	37.7	382
Carbon Tetrachloride	146	250	279	208	2.6
Ethyl Alcohol	2.2	9.7	8.6	8.3	3.0
Xylene	151	171	194	184	-
Reference Fuel B	113	234	273	164	7.0

1. Percent increase in volume after immersion for seven days at ambient temperature.
2. UCC - D_2-carborane-siloxane.
3. General Electric*
4. Dow Corning*
5. Olin Corp.*
6. DuPont*

* Data from "Final Technical Report", Olin Corp. Contract N 00014-71-C-0003.

Our attention next turned to extending fillers which would result in lowering the amount of resin in our formulations without affecting the mechanical properties. Crystalline silicas, Min-U-Sil 5 and Super-Sil, were evaluated. Thus, 30 and 50 phr Silanox 101 with 30 and 50 phr Min-U-Sil 5 and 30 phr Super-Sil were evaluated. Mechanical properties (25 and 300°C) before and after heat aging in air at 315°C are shown in Tables 12, 13, 14, 15, and 16.

The use of 30 phr Silanox 101 with 30-50 phr Min-U-Sil 5 and 30 phr Super-Sil (Tables 13, 14, and 15) have similar or better properties than the sample with only Silanox 101 (Table 12). The sample with 50 phr Silanox 101 and 50 phr Min-U-Sil 5 has significantly less elongation at break (Table 16). This could be counteracted by the use of less peroxide.

The percent volume change after 7 days in toluene was determined as a function of filler content and the results are shown in Table 17. Clearly, more filler decreased volume change. Unfortunately, the acceptable volume change for most military applications is 10-20%; current values are a factor of 10 higher than the desired levels.

Formulations containing 30 phr Silanox 101 and 50 phr Min-U-Sil 5 offer an attractive balance of properties. The tensile strength of 870 psi and elongation of 90% at room temperature fall in the range required for many envisioned high performance elastomer applications. The most obvious advantages associated with the inclusion of extending fillers are the lower systems cost and better solvent resistance.

Evaluation of samples containing 30 phr Silanox 101 and 30 phr magnesium silicate (talc) have been similarly carried out. The data using various grades of magnesium silicate (from Whittaker, Clark, & Daniels, Inc.) are shown in Tables 17, 19, and 20.

After heat aging in air at 315°C, the samples containing Silanox 101 and 505 Talc (Table 18) and the samples containing Silanox 101 and 151 Talc (Table 19) exhibited comparable or better retention of elongation at break (25 and 300°C) than a sample containing only Silanox 101 (Table 12). Changes in modulus and tensile strength were comparable.

TABLE 12

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - 30 PHR SILANOX 101*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	672	1100	466	97	100	30
25	1320	+	304	+	40	+
50	1520	+	407	+	40	+
150	2090	1740	437	180	10	12

* Stock (10352-100) with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not determined.

TABLE 13

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - 30 PHR SILANOX 101/30 PHR MIN-U-SIL 5*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	724	570	743	178	130	40
25	1140	+	570	+	60	+
50	1520	+	578	+	50	+
150	2280	2170	490	293	30	16

* Stock (10352-100) with 30 phr Silanox 101, 30 phr Min-U-Sil 5, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not determined.

TABLE 14

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - 30 PHR SILANOX 101/30 PHR SUPER-SIL*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	772	705	577	100	90	20
25	1430	+	439	+	40	+
50	1710	+	411	+	35	+
150	2660	2000	517	187	30	15

* Stock (10352-100) with 30 phr Silanox 101, 30 phr Super-Sil, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not determined.

- -

TABLE 15

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - 30 PHR SILANOX 101/50 PHR MIN-U-SIL 5*

Aging Time, Hrs.	Young's Modulus psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	890	790	873	184	90	35
25	1985	+	409	+	23	+
50	2567	+	545	+	23	+
150	4569	2910	736	285	18	10

* Stock (10352-100) with 30 phr Silanox 101, 50 phr Min-U-Sil 5, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not determined.

TABLE 16

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - 50 PHR SILANOX 101/50 PHR MIN-U-SIL 5*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	2780	1150	845	183	60	20
25	5117	+	448	+	12	+
50	6823	+	640	+	12	+
150	11,940	3757	501	132	6	4

* Stock (10352-100) with 50 phr Silanox 101, 50 phr Min-U-Sil 5, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not determined.

TABLE 17

VOLUME CHANGE IN TOLUENE*

Phr, Silanox 101	Phr, Min-U-Sil 5	Volume Change**
30	0	161%
30	30	145%
30	50	144%
50	50	112%

* Stock (10352-100) with fillers, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

** Percent volume change in toluene after 7 days at room temperature.

TABLE 18

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - 505 TALC/SILANOX 101*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	820	758	540	86	110	10
25	1230	+	525	+	40	+
50	1430	+	550	+	35	+
150	2250	1960	565	225	25	15

* Stock (10352-100) with 30 phr Silanox 101, 30 phr 505 Talc, and 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not determined.

TABLE 19

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - 151 TALC/SILANOX 101*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	784	635	552	122	95	20
25	930	+	405	+	40	+
50	1690	+	650	+	40	+
150	3090	2470	660	276	20	12

* Stock (10352-100) with 30 phr Silanox 101, 30 phr 151 Talc, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not determined.

TABLE 20

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - 399 TALC/SILANOX 101*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	337	153	362	66	150	60
25	630	--	370	--	60	--
50	1050	--	354	--	40	--
150	1200	2200	330	162	20	8

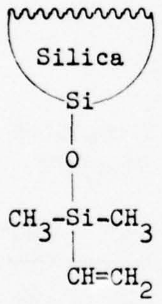
* Stock (10352-100) with 30 phr Silanox 101, 30 phr 399 Talc, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

The results were similar to those obtained using Silanox 101 with Min-U-Sil 5. Thus, a ~25% decrease in carborane-siloxane polymer can be achieved without adversely affecting performance.

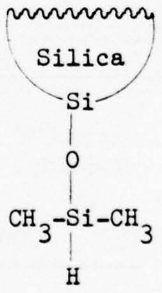
Heat aging data for a sample containing 30 phr Silanox 101 and 30 phr glass fiber (without sizing) are shown in Table 21. Compared to the sample with just Silanox 101 (Table 12), the modulus is increased and the elongation is decreased. This formulation may be important in applications where high modulus is needed; however, currently little value exists for this composition.

4.1.5 Reactive Fillers

To improve the retention of mechanical properties at 300°C, we attempted to increase the amount of resin/filler interaction by using reactive fillers (coupling agents). Thus, samples of reactive fillers were prepared by treatment of Cab-O-Sil with 5% dimethylvinylethoxysilane and 5% dimethylchlorosilane which resulted in silicas with functionalized surfaces - A and B.



Filler A



Filler B

The mechanical properties at 25 and 300°C before and after heat aging in air at 315°C are shown in Tables 22 and 23. Comparison with heat aging data for Silanox 101 (Table 12) showed similar changes in mechanical properties. The modulus and the elongation decreased to a greater extent for the samples with reactive fillers.

Thus, the data does not show any beneficial effects associated with the treated fillers studied.

TABLE 21

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - 30 PHR SILANOX 101/30 PHR GLASS FIBER*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	1830	1930	510	117	45	10
25	2847	--	441	-	17	-
50	4412	--	507	-	12	-
150	9886	7487	913	344	9	5

* Stock (10352-100) with 30 phr Silanox 101, 30 phr glass fiber, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

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TABLE 22

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - Reactive Filler A*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	534	724	409	127	90	20
25	1230	+	225	+	20	+
50	1900	+	300	+	20	+
150	3230	2510	316	138	15	8

* Stock (10352-100) with 30 phr Filler A (Cab-O-Sil pretreated with 5% dimethylvinylethoxysilane), 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not determined.

TABLE 23

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - REACTIVE FILLER B*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	605	578	452	95	100	20
25	1245	+	356	+	40	+
50	2135	+	306	+	25	+
150	3200	2490	409	200	20	10

* Stock (10352-100) with 30 phr Filler B (Cab-O-Sil pretreated with 5% dimethylchlorosilane), 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not determined.

4.1.6 Effect of Molecular Weight

Compounded and cured methylphenylsiloxane modified stocks with molecular weights ranging from 25,600 to 249,000 were evaluated. Using a standard formulation, mechanical properties were determined as a function of molecular weight before and after heat aging in air at 315°C. The data are shown in Tables 24, 25, and 26.

Before heat aging, the materials prepared from the higher molecular weight stocks are tougher, with higher tensile strengths and elongations at break. The higher molecular weight materials are truly superior elastomers. However, after heat aging at 315°C for 25-150 hours, the mechanical properties of all materials converged and showed no significant differences.

Other workers have demonstrated that in the case of polydimethylsiloxane there is a rapid increase in the tensile strength of vulcanizates with increasing stock molecular weight up to a weight of about 400,000.[18] The lack of property dependence on molecular weight in our systems after aging is attributed to the high initial cross-link density of our vulcanizates and the increased cross-linking during aging. Thus, molecular weight effects diminish as the cross-link density increases. At the other extreme, where the stocks are uncross-linked, there are very major differences in the performance characteristics of the elastomers with the 249,000 $\bar{M}_w$ stock exhibiting excellent elastomeric properties (see Tables 6 and 7).

From these studies it was concluded that our high molecular weight stocks should be less cross-linked initially. This can be achieved by reducing the vinyl content of the base stock or by adding less peroxide. Thus, improved retention of properties after aging should result.

4.1.7 Peroxide Content

In the previous section of this report it was concluded that the vulcanizates should be less cross-linked. Indeed, problems have been encountered in curing thick specimens of stock and over-cross-linking due to excess peroxide appeared to be responsible. Therefore, a

TABLE 24

TENSILE STRENGTH AS A FUNCTION OF MOLECULAR WEIGHT*

Aging Time (hrs.)	$\bar{M}_w$		
	25,600	113,000	249,000
0	330 psi	580 psi	643 psi
25	610 psi	610 psi	536 psi
50	510 psi	550 psi	519 psi
75	--	620 psi	437 psi
150	520 psi	450 psi	876 psi

* Mechanical properties measured at 25°C after heat aging in air at 315°C. Stocks (33 mole % methylphenyl modified) with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

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TABLE 25

MODULUS AS A FUNCTION OF MOLECULAR WEIGHT*

Aging Time (hrs.)	$\bar{M}_w$		
	25,600	113,000	249,000
0	550 psi	560 psi	657 psi
25	1490 psi	1490 psi	1095 psi
50	1510 psi	2030 psi	1298 psi
75	--	2760 psi	1704 psi
150	3410 psi	3330 psi	6200 psi

* See footnote in Table 24.

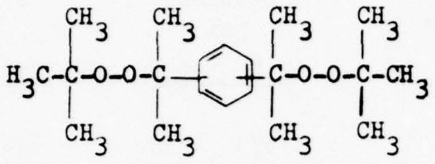
TABLE 26

ELONGATION AT BREAK AS A FUNCTION OF MOLECULAR WEIGHT*

Aging Time (hrs.)	$\bar{M}_w$		
	25,600	113,000	249,000
0	70%	135%	110%
25	50%	50%	55%
50	30%	35%	40%
75	-	30%	30%
150	20%	20%	20%

* See footnote in Table 24.

systematic evaluation of mechanical properties as a function of peroxide content was carried out. Properties at 25 and 300°C for samples containing various levels of dicumyl peroxide and Vul Cup R are shown in Tables 27 and 28.



Vul Cup R

The amount of dicumyl peroxide and Vul Cup R was varied from 1.0 to 3.0 phr and 0.7 to 3.0 phr, respectively.

Perusal of the data indicate that: (1) the initial modulus decreased and the elongation increased as the peroxide level decreases; (2) with Vul Cup R, the tensile strength increased with a decrease in peroxide; and (3) there is a reduction in the loss of mechanical properties on aging as the peroxide content is reduced. Presently, 1.0 to 1.5 phr peroxide appears to represent an optimum peroxide level. The improved retention of properties with aging provides the greatest incentive for employing the optimal peroxide concentration.

The study has afforded valuable information leading to both improvements in mechanical aging properties and fabrication characteristics. Void-free plaques which are 1/8" in thickness have been prepared without difficulty at the lower peroxide levels.

4.1.8 Antioxidant - Ferric Oxide

Ferric oxide is a standard antioxidant in silicone rubber technology.[19] The usefulness in carborane-siloxane elastomers has been previously demonstrated.[8] The antioxidant effect of ferric oxide has been postulated to occur by the oxidation of the propagating species, R·, by ferric ion.[20]

$$Fe^{+3} + R\cdot \longrightarrow R^{+} + Fe^{+2}$$

TABLE 27

EFFECT OF PEROXIDE LEVEL ON MECHANICAL PROPERTIES* DICUMYL PEROXIDE

Amount Peroxide, phr	Heat Aging Time,** Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
		25°	300°	25°	300°	25°	300°
3.0	0	573	553	594	111	135	25
3.0	25	1,570	+	360	+	35	+
3.0	150	13,000	4,770	930	213	11	4
2.5	0	553	511	691	121	160	30
2.5	25	1,530	+	400	+	40	+
2.5	150	4,700	3,670	500	150	15	4
2.0	0	514	457	694	88	185	24
2.0	25	940	+	345	+	45	+
2.0	150	3,500	3,100	390	197	16	8
1.5	0	411	411	573	110	190	35
1.5	25	870	+	280	+	50	+
1.5	150	1,900	1,650	310	140	23	10
1.0	0	401	382	559	73	205	25
1.0	25	800	+	340	+	70	+
1.0	150	2,100	1,380	320	120	27	10

* Stock (33 mole % methylphenyl) with 30 phr Silanox 101, 2.5 phr ferric oxide, and peroxide as indicated.

** Heat aged in air at 315°C.

\+ Not determined.

TABLE 28

EFFECT OF PEROXIDE LEVEL ON MECHANICAL PROPERTIES* VUL CUP R

Amount Peroxide, phr	Heat Aging Time,** Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
		25°	300°	25°	300°	25°	300°
3.0	0	760	665	456	46	80	8
3.0	25	1,380	+	350	+	30	+
3.0	150	145,000	11,700	2,670	190	1	2
2.5	0	604	553	450	35	105	6
2.5	25	1,190	+	310	+	35	+
2.5	150	46,000	6,200	1,570	249	10	4
2.0	0	587	593	528	90	120	19
2.0	25	1,150	+	520	+	50	+
2.0	150	39,000	5,260	1,630	241	13	4
1.5	0	470	540	605	123	135	29
1.5	25	980	+	270	+	40	+
1.5	150	4,900	3,260	530	150	20	5
1.0	0	433	370	618	79	170	26
1.0	25	700	+	225	+	40	+
1.0	150	2,700	1,300	330	130	20	7
0.7	0	270	285	678	63	220	27
0.7	25	710	+	470	+	80	+
0.7	150	2,500	1,600	420	166	25	10

* Stock (33 mole % methylphenyl) with 30 phr Silanox 101, 2.5 phr ferric oxide, and peroxide as indicated.

** Heat aged in air at 315°C.

\+ Not determined.

Normally powdered ferric oxide (2.5 phr) is added during compounding. However, R. S. Neale and A. N. Pines have reported an improved preparation of ferric oxide from iron pentacarbonyl which is apparently homogeneous in silicone oils and results in better antixoidant efficiencies.[21] Therefore, samples of carborane-siloxane elastomer were prepared containing finely dispersed ferric oxide. The mechanical properties before and after heat aging (at 315°C) in air are shown in Tables 29 and 30 can be compared with results using powdered ferric oxide (2.5 phr) shown in Table 12. Method A employed a solvent during formulation (.05 phr) and Method B did not (2.5 phr).

Clearly, the use of highly dispersed ferric oxide perpared by Method A (Table 29) showed definite advantages over powdered ferric oxide (Table 30). More significantly, however, is the considerably improved effectiveness. The samples in Table 12 contain 2.5 phr ferric oxide powder and the samples in Table 30 contain only 0.05 phr finely dispersed ferric oxide.

4.2 Evaluation of Property Loss During Heat Aging

From previous heat aging studies[8] at 315°C (600°F) it was concluded that in air the elastomer was becoming more cross-linked and that in nitrogen the loss of properties could be attributed to chain scission. In order to corroborate these conclusions the cross-link density as measured by the volume change after immersion in a good solvent was determined. Results are summarized in Tables 31 and 32, along with the associated mechanical properties. Heat aging in air results in an increase in modulus and tensile strength and a decrease in elongation. Clearly, the material is becoming more cross-linked.

In nitrogen, the samples exhibited a decrease in modulus, tensile strength and elongation. The nitrogen results were interpreted to indicate that the polymer was undergoing a small amount of depolymerization or uncross-linking at 315°C. This is suggestive that the cross-linked moieties (from methylvinylsilane) as shown below, or bonds in the polymer backbone, were probably breaking.

TABLE 29

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - FERRIC OXIDE - METHOD A*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	870	330	600	42	270	30
25	874	+	485	+	80	+
50	965	+	530	+	70	+
150	1214	1010	400	140	40	15

* Stock (10352-100) with 30 phr Silanox 101, .05 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not determined.

- -

TABLE 30

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR (315°C) - FERRIC OXIDE - METHOD B*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	960	890	475	63	105	20
25	21,000	+	950	+	10	+
50	149,000	+	560	+	3	+
150	149,000	**	210	**	0.2	**

* Stock (10352-100) with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

** Too brittle to measure.

\+ Not determined.

TABLE 31

PROPERTIES AT 25°C AFTER HEAT AGING AT 315°C*

Aging Time, Hrs.	Air				Nitrogen			
	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %	Volume Change,** %	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %	Volume Change,** %
0	533	613	100	88	1,000	950	110	88
25	922	442	60	94	670	520	80	110
50	1,117	427	55	65	670	420	60	105
75	1,311	485	50	67	670	300	50	104
150	1,813	533	45	68	670	220	40	97
300	3,400	570	30	+	+	+	+	+

* Stock 10352-7 (33 mole % diphenylsiloxane modified) with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

** ASTM test method D471-72 samples were immersed 7 days in benzene at room temperature.

\+ Not determined.

TABLE 32

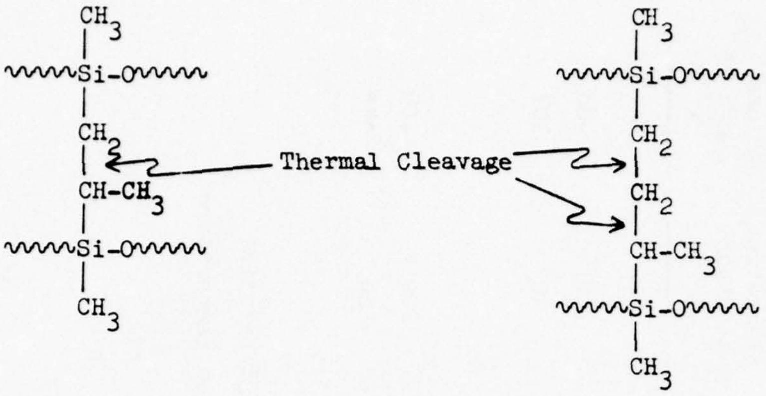
PROPERTIES AT 25°C AFTER HEAT AGING AT 315°C*

Aging Time, Hrs.	Air				Nitrogen			
	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %	Volume Change,** %	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %	Volume Change,** %
....33 mole % diphenyl/4 mole % methylvinyl....								
0	533	613	100	88	1,000	950	110	88
150	1,813	533	45	68	670	220	40	107
....67 mole % methylphenyl....								
0	287	283	220	209	287	283	220	209
150	1,220	400	60	101	133	12	20	***

* Stock with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

** ASTM test method D471-72 samples were immersed 7 days in benzene at room temperature.

*** Sample disintegrates.



A key experiment was performed in which the D_2-carobrane-dimethyl/methylphenylsiloxane (33/67) stock was heat aged in nitrogen at 315°C for 100 hours. The relative viscosity after heat aging was almost identical to the relative viscosity before heat aging (Table 33).

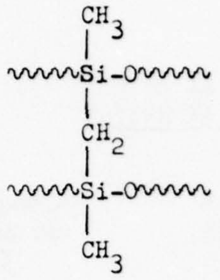
TABLE 33

RELATIVE VISCOSITY - HEAT AGING

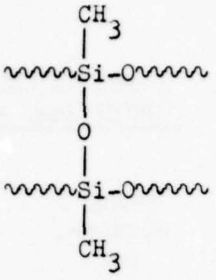
	R.V. dl/g ($CHCl_3$)	$\bar{M}_w$
Before	0.42	98,000
After	0.39	92,000

Clearly, the stock backbone is not undergoing any significant amount of bond cleavage during this heat aging study. The loss of mechanical properties observed with the cured stock must therefore be due mostly to thermal breaking of the cross-linking bonds.

Future work will be directed towards preparing elastomers with only one carbon atom in the cross-linking moiety or a siloxane link. These compositions are attainable through silyl hydride moieties on the polymer backbone.



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \sim\sim\mathrm{Si{-}O}\sim\sim \\ | \\ \mathrm{CH_2} \\ | \\ \sim\sim\mathrm{Si{-}O}\sim\sim \\ | \\ \mathrm{CH_3} \end{array}$$



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \sim\sim\mathrm{Si{-}O}\sim\sim \\ | \\ \mathrm{O} \\ | \\ \sim\sim\mathrm{Si{-}O}\sim\sim \\ | \\ \mathrm{CH_3} \end{array}$$

Compounded and cured samples with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide were heat aged at 343 and 371°C. Samples prepared from 33 mole % diphenylsiloxane modified stock are shown in Tables 34 and 35. Samples prepared from 33 mole % and 67 mole % methylphenylsiloxane modified stock are shown in Tables 36 and 37, respectively.

At 343°C the diphenylsiloxane modified material shows superior heat aging properties. Moreover, there is a much more rapid loss of mechanical properties at 343°C than at 315°C. After 300 hours at 315°C in air the modulus increased from 533 to 3,400 psi, the tensile strength decreased slightly from 613 to 570 psi, and the elongation at break decreased from 100 to 30%. After 16 hours at 371°C in air, samples were too brittle for measurements. These results indicate that UCARSIL should be rated as a 300-340°C elastomer.

Further studies are warranted on the maintenance of mechanical properties upon heat aging in air at 343 and 371°C. The results also demonstrate the desirability of replacing the central silylmethyl units in our repeat unit with silylphenyl moieties.

4.3 D_2-Carborane-methyltrifluoropropylsiloxane

Compounded and cured D_2-carborane-dimethyl/methylphenylsiloxane (67/33 mole %) exhibited large swelling in certain solvents (i.e., CCl_4, reference fuel B, toluene, etc.; see Table 10). Some military applications require high temperature sealants which have low swell ratios in jet fuels; therefore, the methyltrifluoropropylsiloxane modified stock (10352-125-1) was prepared in order to improve the solvent resistance. The structure is shown in Figure 17. This material has a Tg of -29°C (via DSC). The molecular weight employed in these studies was 220,000

TABLE 34

MECHANICAL PROPERTIES AT 25°C AFTER HEAT AGING IN AIR AT 343°C*

Aging Time, Hrs.	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break %
0	430	740	220
4	460	739	125
16	952	503	50
24	1140	293	30

* Stock (33 mole % diphenylsiloxane) with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

- -

TABLE 35

MECHANICAL PROPERTIES AT 25°C AFTER HEAT AGING IN AIR AT 371°C*

Aging Time, Hrs.	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %
0	430	740	220
4	15,600	839	15
16	**	**	**

* See footnote in Table 31.

** Too brittle to measure.

TABLE 36

MECHANICAL PROPERTIES AT 25°C AFTER HEAT AGING IN AIR AT 343°C*

Aging Time, Hrs.	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %
0	460	505	220
4	1,230	516	50
16	91,000	1,800	5
24	163,000	2,930	4

* Stock (33 mole % methylphenylsiloxane) with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

- -

TABLE 37

MECHANICAL PROPERTIES AFTER HEAT AGING IN AIR*

Aging Time, Hrs.	Aging Temp., °C	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
		25°	300°	25°	300°	25°	300°
0	--	287	94	283	43	220	60
150	315	1220	840	400	92	60	10
24	343	1780	+	490	+	35	+
24	371	**	+	**	+	**	+

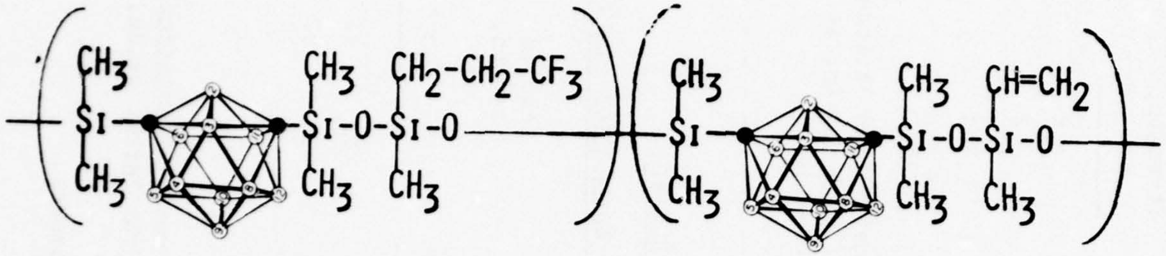
* Stock (67 mole % methylphenylsiloxane) with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

** Too brittle to measure.

\+ Not determined.

FIGURE 17

D_2-CARBORANE-METHYLTRIFLUOROPROPYLSILOXANE (WITH 4 MOLE % METHYLVINYLSILOXANE)



TG = -29°C

($\bar{M}_W$ = 220,000)

(via GPC). The thermogravimetric analysis is shown in Figure 18 and is compared with the methylphenylsiloxane modified stock. Clearly, the methyltrifluoropropylsiloxane moieties are not stable at 300°C. This weight loss occurring around 300°C and leveling off at 350°C corresponds to the loss of HF. The TGA in air and nitrogen is shown in Figure 19.

Mechanical properties, as a function of temperature for samples containing Silanox 101 and Cab-O-Sil as reinforcing fillers, are shown in Tables 38 and 39. At low temperatures (-20 and -30°C), the properties change markedly due to a glass transition temperature of -29°C.

TABLE 38

MECHANICAL PROPERTIES VS. TEMPERATURE - CARBORANE-METHYLTRIFLUOROPROPYLSILOXANE/SILANOX 101*

Temp., °C	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %
290	408	52	15
260	420	92	30
200	489	149	40
25	783	540	100
-20	21,400	1,130	15
-30	221,000	2,470	2

* Carborane-methyltrifluoropropylsiloxane with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

- -

The thermal instability is reflected in the rapid change in mechanical properties after heat aging in air at 315°C for 25 hours (Table 40).

TABLE 39

MECHANICAL PROPERTIES vs. TEMPERATURE - CARBORANE-METHYLTRIFLUOROPROPYLSILOXANE/CAB-O-SIL*

Temp. °C	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %
290	1,230	160	20
260	1,130	98	10
200	1,350	205	20
25	1,120	640	110
-20	22,200	1,250	15
-30	115,000	2,970	3

* Carborane-methyltrifluoropropylsiloxane with 30 phr Cab-O-Sil, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

- -

TABLE 40

MECHANICAL PROPERTIES AT 25°C AFTER HEAT AGING IN AIR AT 315°C*

Aging Time, min.	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %
0	783	540	100
25	7,400	200	2

* Carborane-methyltrifluoropropylsiloxane with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

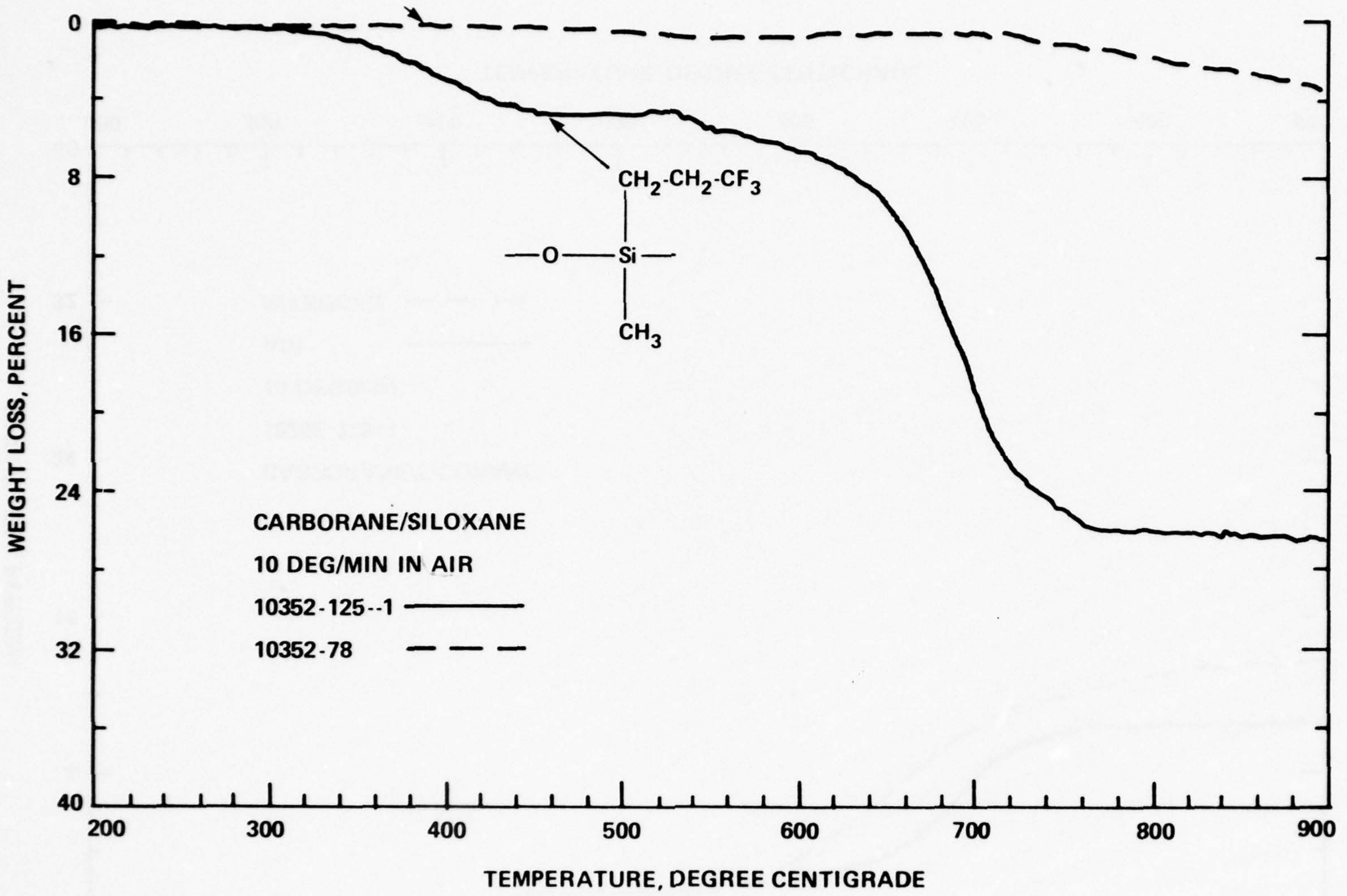


FIGURE 18. TGA IN AIR :

D_2-CARBORANE-DIMETHYL/PHENYLMETHYLSILOXANE (67/33)

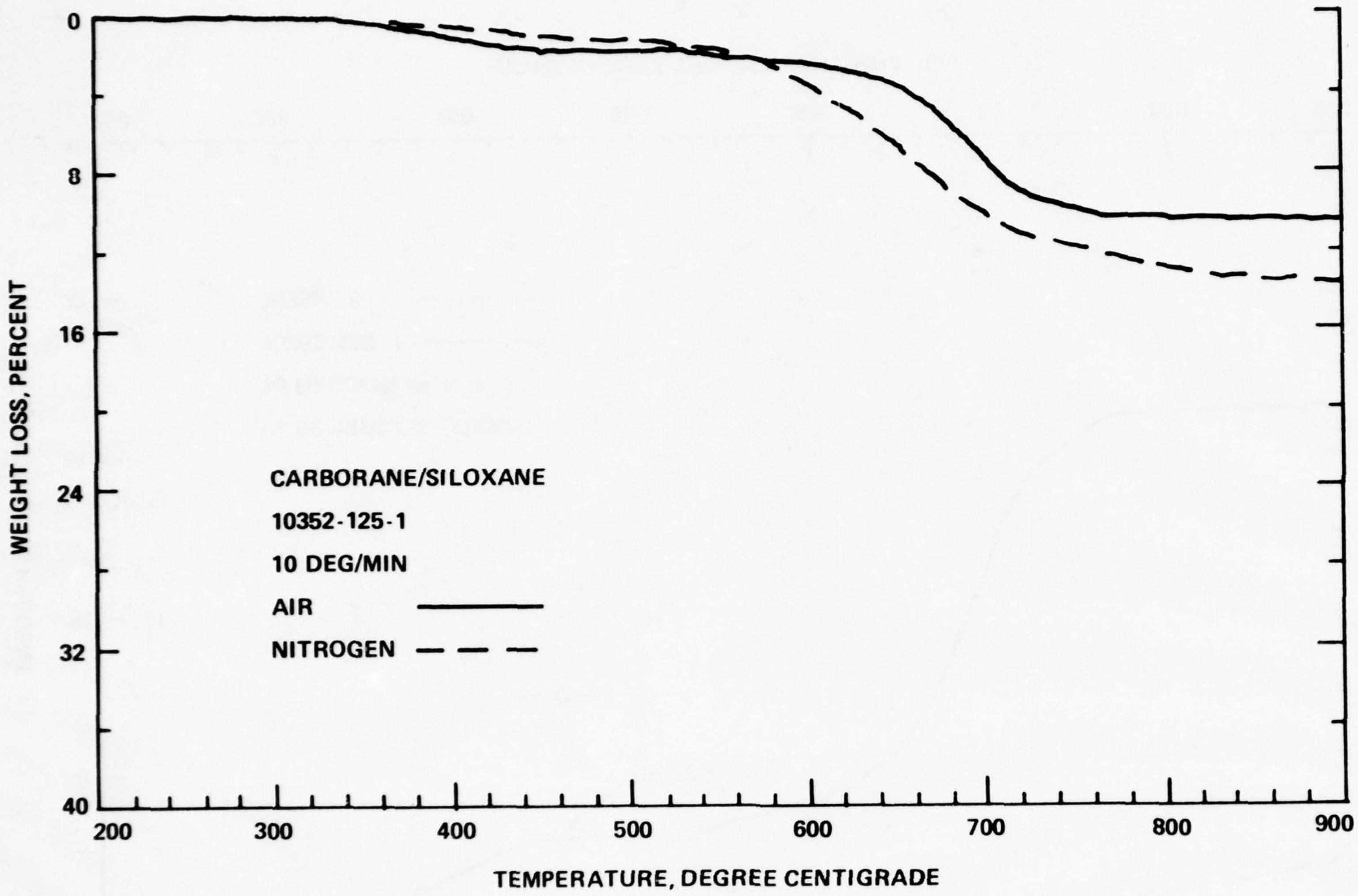


FIGURE 19. TGA: AIR AND NITROGEN

A loss of 30-50°C in thermal stability would probably be acceptable if there was an associated marked improvement in the swelling ratio in jet fuel. Therefore, heat aging studies in air were carried out at 290°C. The results using two different fillers are shown in Tables 41 and 42.

This material remains elastomeric after 150 hours at 290°C. The deleterious effect of Cab-O-Sil on the phenylsiloxane modified stocks is not apparent in this system. The upper use temperature for this stock would be $\lesssim$290°C.

Following ASTM test method D 471-72 (immersion for seven days at ambient temperatures), mechanical properties before and after solvent exposure are shown in Tables 43 and 44 for specimens containing Silanox 101 and Cab-O-Sil. The samples with Silanox 101 are affected more by the solvent than the samples with Cab-O-Sil.

The percent swelling is compared with data for the 33 mole % methylphenyl modified material in Table 45. The samples with Cab-O-Sil have lower swelling; however, values of 10-20% are required in fuel tank sealant applications. Thus, the trifluoropropyl modified stock in Figure 17 does not meet the desired solvent resistance goals.

Further improvements are noted by the addition of 50 phr Cab-O-Sil and 50 phr Min-U-Sil 5 (Table 46). Future work in this area will be directed towards samples prepared from bis-(hydroxymethyltrifluoropropylsilyl)-meta-carborane.

4.4 Surface Fluorination

In the preceding section efforts were described to improve solvent resistance by the incorporation of trifluoropropyl groups. The results demonstrated the utility of fluorocarbon moieties. An alternative approach has been studied in which the surface of the vulcanizate has been fluorinated. Such surface fluorination has been performed using molecular fluorine in nitrogen. A lightly fluorinated material is characterized by 0.3% weight gain and 43 micrograms of fluorine per square centimeter. Medium fluorination corresponds to 0.4% weight gain at 68 micrograms of fluorine per square centimeter.

Mechanical properties before and after heat aging in air at 290°C are shown in Table 47. The fluorination appears to have no great effect on the retention of properties after heat aging.

TABLE 41

HEAT AGING STUDIES (290°C IN AIR)
CARBORANE-METHYLTRIFLUOROPROPYLSILOXANE/SILANOX 101*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	290°	25°	290°	25°	290°
0	783	408	540	52	100	15
25	509	+	148	+	40	+
150	5600	2420	380	128	10	4

* Carborane-methyltrifluoropropylsiloxane with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not measured.

TABLE 42

HEAT AGING STUDIES (290°C IN AIR)
CARBORANE-METHYLTRIFLUOROPROPYLSILOXANE/CAB-O-SIL*

Aging Time, Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
	25°	290°	25°	290°	25°	290°
0	1120	1230	640	160	110	20
25	1620	+	402	+	60	+
150	4100	3190	426	97	15	3

* Carborane-methyltrifluoropropylsiloxane with 30 phr Cab-O-Sil, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

\+ Not measured.

TABLE 43

SOLVENT RESISTANCE - MECHANICAL PROPERTIES*
CARBORANE-METHYLTRIFLUOROPROPYLSILOXANE/SILANOX 101

Solvent**	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break %	Swell, %
None	783	540	100	--
Methanol	226	298	155	1.5
Toluene	484	497	280	129
Acetone	1030	95	65	71
CCl_4	797	407	190	121
Reference Fuel B	755	189	120	100

* Carborane-methyltrifluoropropylsiloxane with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

** ASTM test method D 471-72 immersed seven days at room temperature.

- -

TABLE 44

SOLVENT RESISTANCE - MECHANICAL PROPERTIES*
CARBORANE-METHYLTRIFLUOROPROPYLSILOXANE/CAB-O-SIL

Solvent**	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %	Swell, %
None	1120	640	110	--
Toluene	1566	677	145	98
Acetone	1454	671	145	2.3
Reference Fuel B	1600	603	120	80

* Carborane-methyltrifluoropropylsiloxane with 30 phr Cab-O-Sil, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

** ASTM test method D 471-72 immersed seven days at room temperature.

TABLE 45

PERCENT SWELLING*

Solvent	Stock/Filler**		
	33% Methylphenyl	Methyltrifluoropropyl	
	Silanox 101	Silanox 101	Cab-O-Sil
Methanol	1.7	1.5	--
Toluene	162	129	98
Acetone	49	71	2.3
CCl_4	146	121	--
Reference Fuel B	113	100	80

* ASTM test method D 471-72 immersed seven days at room temperature.

** Stocks with 30 phr filler, 2.5 phr ferric oxide, 2.5 phr dicumyl peroxide.

- -

TABLE 46

SOLVENT RESISTANCE - MECHANICAL PROPERTIES*
50 PHR CAB-O-SIL/50 PHR MIN-U-SIL

Solvent**	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %		Swell, %
	25°	290°	25°	290°	25°	290°	
None	8650	4060	570	300	33	10	--
Toluene	10280	4310	660	176	40	5	50
Reference Fuel B	7450	4530	274	399	10	15	48

* Carborane-methyltrifluoropropylsiloxane with 50 phr Cab-O-Sil, 50 phr Min-U-Sil, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

** ASTM test method D 471-72 immersed seven days at room temperature.

TABLE 47

SURFACE FLUORINATION - MECHANICAL PROPERTIES*

Surface Fluorination	Heat Aging Time,** Hrs.	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %	
		25°	290°	25°	290°	25°	290°
None	0	800	726	604	146	120	26
	25	3600	2670	620	70	25	2
Light	0	1070	727	495	80	110	10
	25	2400	2900	557	158	40	6
Medium	0	1180	844	642	82	120	10
	25	2600	2900	543	38	30	1

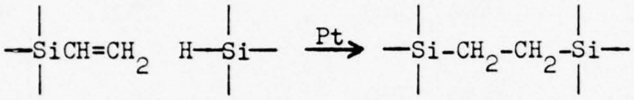
* Stock (33 mole % methylphenyl) with 30 phr Silanox 101, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide.

** Samples were heat aged in air at 290°C.

Solvent resistance in toluene is shown in Table 48. Hence, the levels of fluorination used have no significant effect on the solvent resistance. Higher levels of fluorination may be necessary.

4.5 RTV Systems

To develop a room temperature vulcanizing (RTV) system for use in coatings, sealants and potting compounds, the cure of vinyl modified D_2-carborane-siloxane stock with silyl hydrides was evaluated. Conventional polydimethylsiloxanes containing vinyl moieties can be cured at room temperature with silyl hydride using chloroplatinic acid as a catalyst.



$$-\overset{|}{\underset{|}{Si}}CH=CH_2 \quad H-\overset{|}{\underset{|}{Si}}- \xrightarrow{Pt} -\overset{|}{\underset{|}{Si}}-CH_2-CH_2-\overset{|}{\underset{|}{Si}}-$$

Blends of methylphenyl modified stocks containing 4 mole % methylvinylsiloxane and methyl-H-siloxane were evaluated. A 50:50 blend of the above containing 30 phr Silanox 101, 2.5 phr ferric oxide and 10 ppm platinum (in the form of chloroplatinic acid) exhibited no cure after 18 hours. However, the material appeared to have cured slightly after 72 hours at 90°C. When the platinum level was increased to 1.2×10^4 ppm, the material cured overnight. Mechanical properties are listed in Table 49.

After heat aging 25 hours in air, the material became too brittle to measure. This high level of platinum may be causing the polymer to undergo excessive cross-linking.

The reaction of diphenylsilane with methylvinylsiloxane stock was also evaluated.

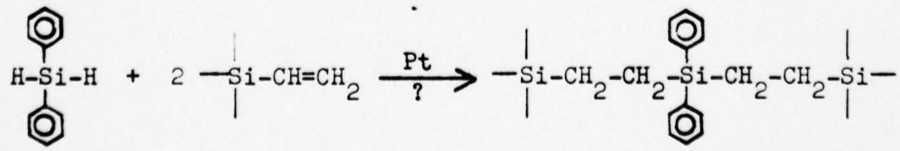


TABLE 48

SURFACE FLUORINATION - SOLVENT RESISTANCE*

Surface Fluorination	Young's Modulus, psi		Tensile Strength, psi		Elongation at Break, %		Swell, %
	25°	290°	25°	290°	25°	290°	
None	640	705	288	59	85	10	115
Light	750	782	374	67	110	10	115
Medium	855	822	454	88	110	10	111

* ASTM test method D 471-72 immersed seven days at room temperature in toluene.

TABLE 49

MECHANICAL PROPERTIES FOR RTV SYSTEM*

Heat Aging Time,** Hrs.	Young's Modulus psi		Tensile Strength, psi		Elongation at Break, %	
	25°	300°	25°	300°	25°	300°
0	190	6187	602	49	320	2
25	+		+		+	

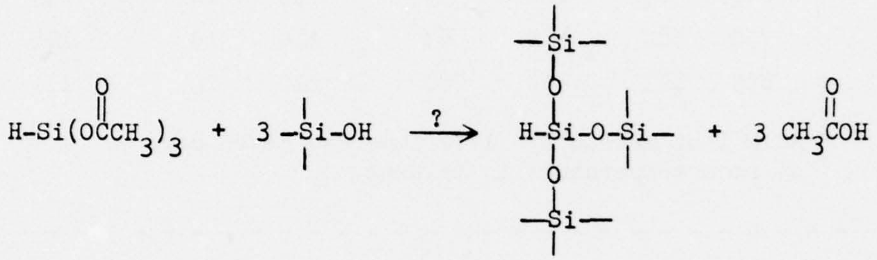
* Stock with 30 phr Silanox 101, 2.5 phr ferric oxide and 1.2 x 10^4 ppm platinum.

** Heat aged at 315°C in air.

\+ Too brittle to measure.

With 10 ppm platinum, no curing was observed after 18 hours at room temperature or 90°C. Hence, these systems exhibit very little activity at these low levels of platinum and high activity with high levels of platinum. Further optimization is needed.

The reaction of triacetoxysilane with carborane silanol terminated stock showed no cure after 18 hours at room temperature and only slight curing after 18 hours at 90°C.



$$\mathrm{H{-}Si(O\overset{\overset{O}{\|}}{C}CH_3)_3} + 3\,{-}\overset{|}{\underset{|}{\mathrm{Si}}}{-}\mathrm{OH} \xrightarrow{?} \mathrm{H}{-}\overset{\overset{{-}\overset{|}{\mathrm{Si}}{-}}{\overset{|}{\mathrm{O}}}}{\underset{\underset{{-}\underset{|}{\mathrm{Si}}{-}}{\underset{|}{\mathrm{O}}}}{\mathrm{Si}}}{-}\mathrm{O}{-}\overset{|}{\underset{|}{\mathrm{Si}}}{-} + 3\,\mathrm{CH_3\overset{\overset{O}{\|}}{C}OH}$$

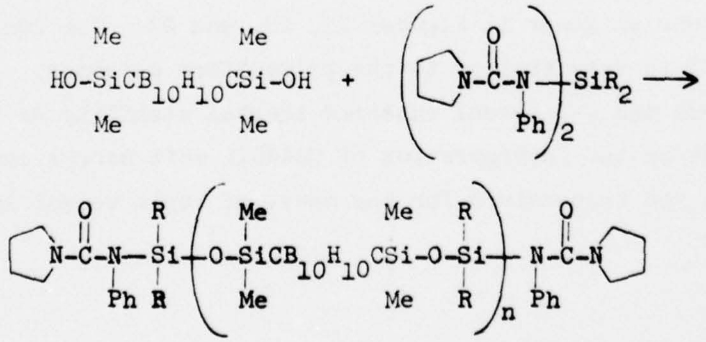
Similar results were obtained with triethoxysilane. Thus, the carborane silanol does not appear to be reactive towards conventional trisubstituted RTV agents.

5.0 BLOCK COPOLYMERS

The development of thermoplastic elastomers represents one of the most significant contributions to the science and technology of materials in the last decade. Advantages of block copolymer elastomers vis-à-vis vulcanized counterparts include their greater versatility, the ease of processing and potential for use of scrap, and excellent mechanical properties; the major disadvantage is the rapid decrease in mechanical properties as the temperature approaches the Tg of the hard block.

A great incentive exists for developing thermoplastic elastomers which combine the elastomeric capabilities of the D_2-carborane-siloxane elastomers with the mechanical performance and solvent resistance of polyimides, polyarylethers and other super performance rigid materials, without compromising the thermal capabilities of either system. In addition to the advantages of thermoplastic elastomers described above, it can be projected that D_2-carborane-siloxane/polyimide $(AB)_n$ block copolymers will exhibit excellent solvent resistance, continuous performance between ~ -30°C and >300°C, and cost effectiveness.

Condensation of the bis-(ureidosilane)-terminated carborane-siloxane oligomers, prepared as shown below, with a second suitably terminated (hydroxyl, silanol, etc.) oligomer should afford the corresponding block copolymer.



Through the proper selection of rigid A blocks and elastomeric B blocks, new copolymers possessing all the advantages associated with thermoplastics (short fabrication cycles, reprocessability) and carborane-siloxane polymers (thermal stability), should be available. Initial studies have been carried out using dihydroxy terminated polysulfone oligomers (Figure 20). An alternative method was also investigated in which the polysulfone oligomer was added to excess bis-(ureidosilane), followed by slow addition of carborane disilanol (10615-33). However, this resulted in a very hard, brittle material. Clearly, the method shown in Figure 20 is the preferred route.

Properties of UCARSIL block copolymers, prepared using urea terminated UCARSIL oligomers are shown in Table 50. All block copolymers have molecular weights around 100,000. Block copolymer 10615-41 has a very high elongation; however, its modulus and tensile strength are low. This can be overcome by optimizing the molecular weights of the individual blocks. The hard sulfone block is responsible for reinforcing the elastomer block in these type systems.

All copolymers have an ~6,000 molecular weight hard sulfone block; 10615-41 and 10615-35 have soft UCARSIL blocks of ~12,000 and ~30,000 molecular weight ($\bar{M}_n$), respectively. Since UCARSIL blocks with $\bar{M}_n$ ~10-15,000 should be preferred, future studies will emphasize their incorporation.

These results demonstrate the feasibility of applying the UCARSIL polymerization technology to the preparation of thermoplastic block copolymer elastomers. Additional work is planned.

Thermogravimetric analysis of 10615-33, -35, and -41 are compared with the polysulfone oligomer in Figures 21, 22, and 23. The TGA of copolymer 10615-33 is very similar to the polysulfone oligomer. However, the TGA of 10615-35 and -41 reveal enhanced thermal stability as compared to the polysulfone by the incorporation of UCARSIL soft blocks into the polymer. Indeed, the temperature for the onset of rapid weight loss is increased by 80°C.

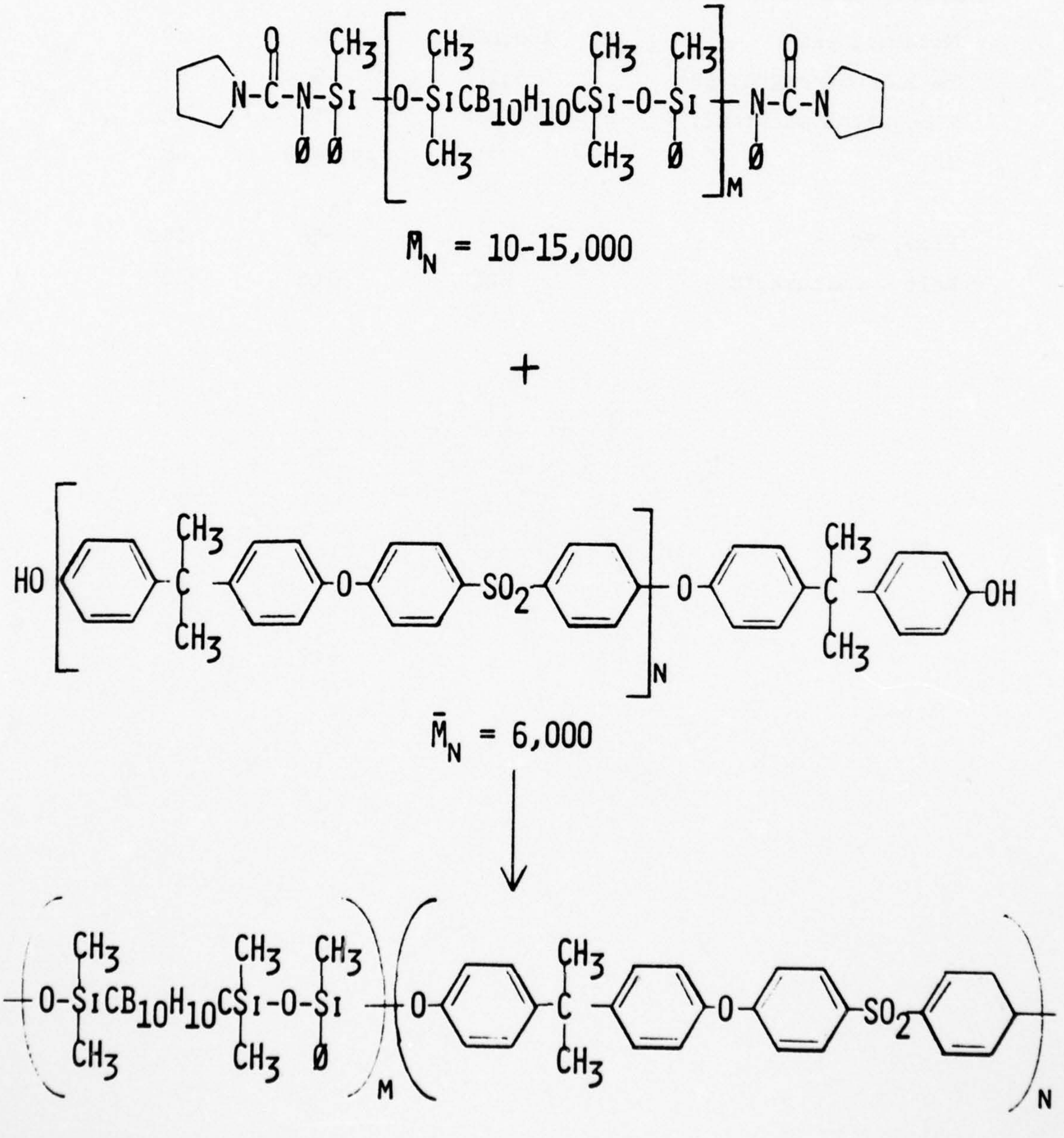
TABLE 50

PROPERTIES OF UCARSIL BLOCK COPOLYMERS

Property	10615-		
	33	35	41
Modulus, psi	160,000	85	20
Tensile Strength, psi	5,100	9	45
Elongation at Break, %	4	15	225
Tg, °C	144	-5, +24	-8
Flow, °C	~190	~70	~100
Melt - Failure,°C	~260	~165	~130

FIGURE 20

COPOLYMER DERIVED FROM UCARSIL AND POLYSULFONE



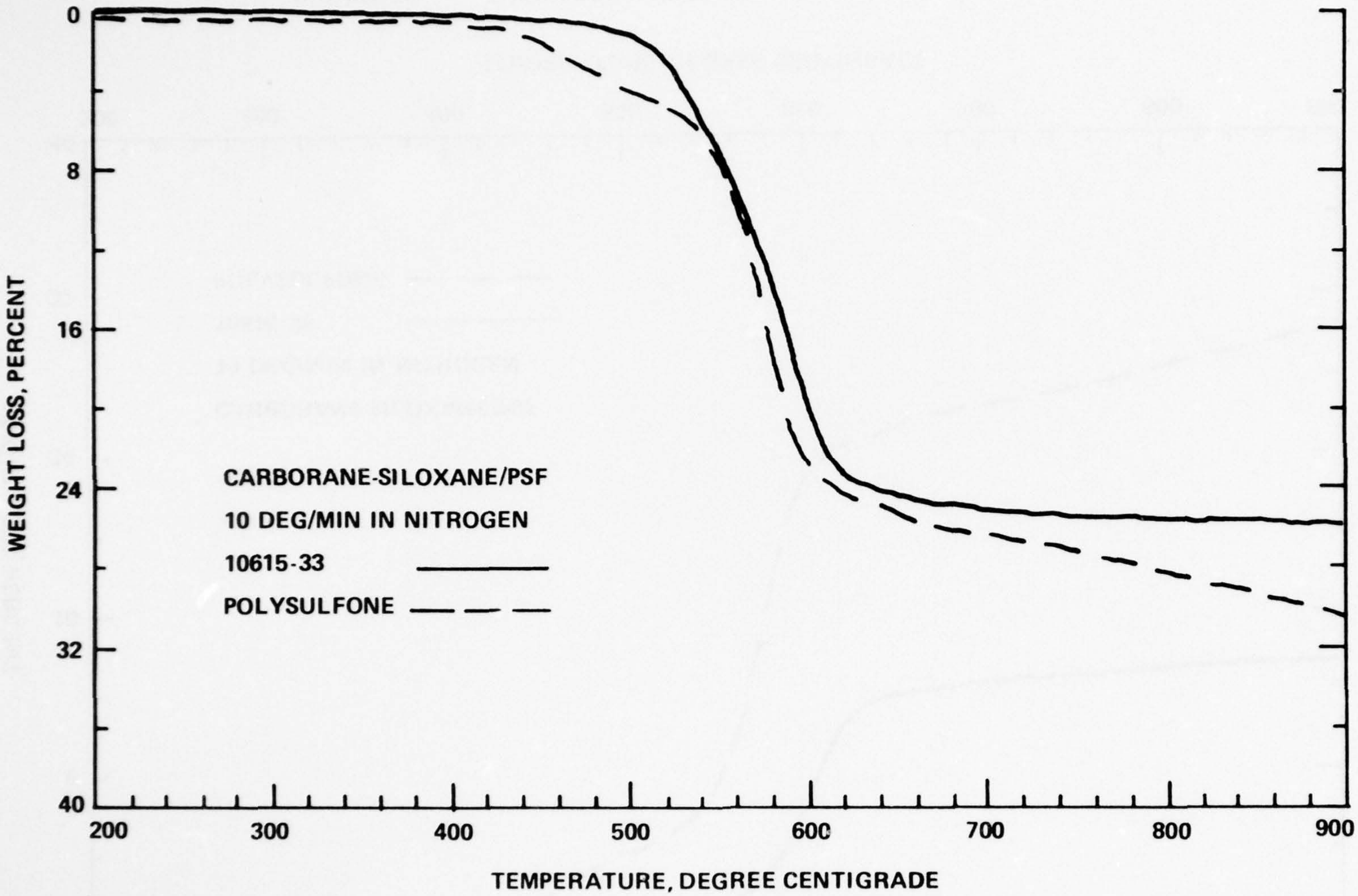


FIGURE 21. THERMOGRAVIMETRIC ANALYSIS OF UCARSIL BLOCK COPOLYMER (10615-33)

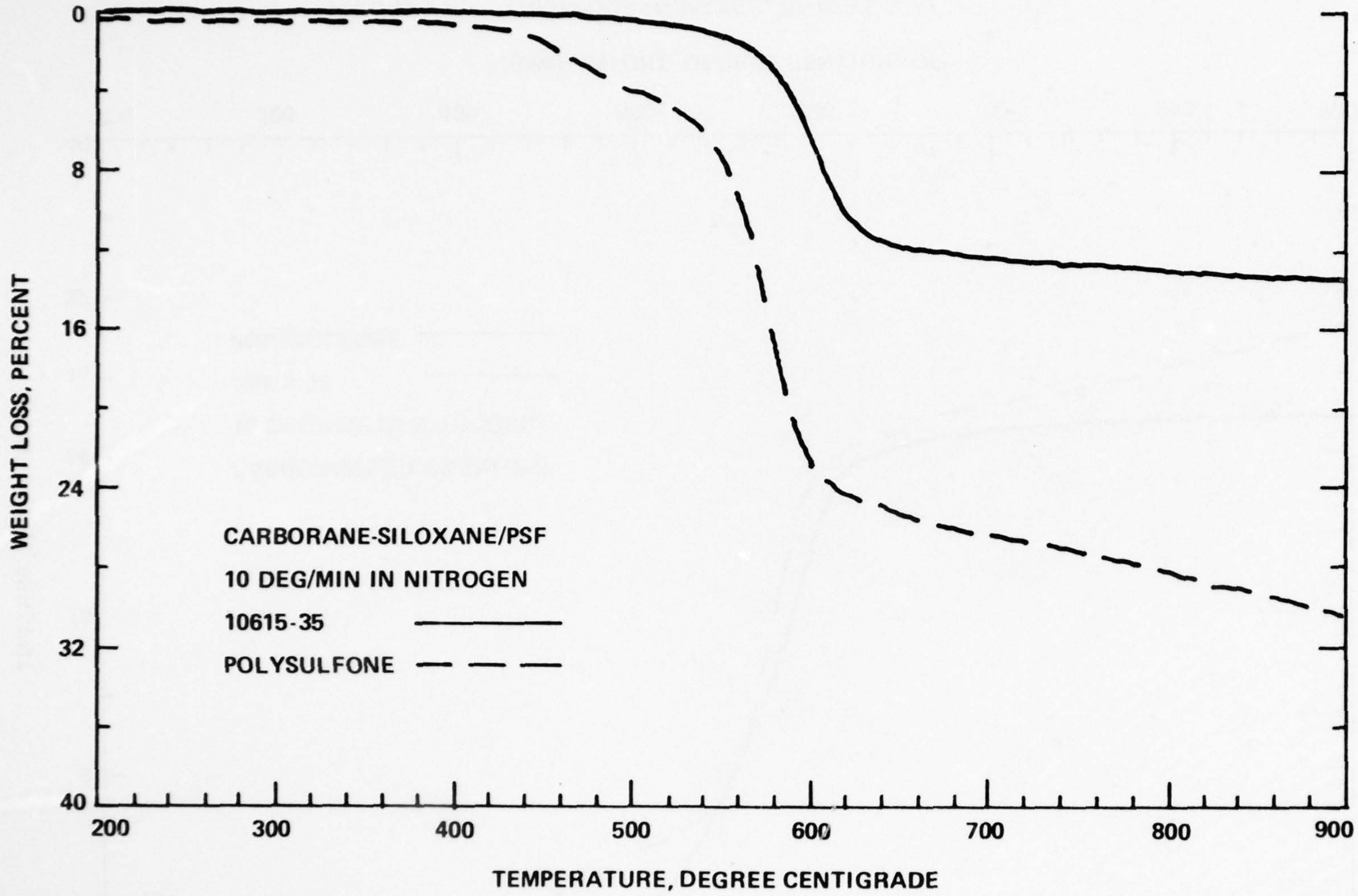


FIGURE 22. THERMOGRAVIMETRIC ANALYSIS OF UCARSIL BLOCK COPOLYMER (10615-35)

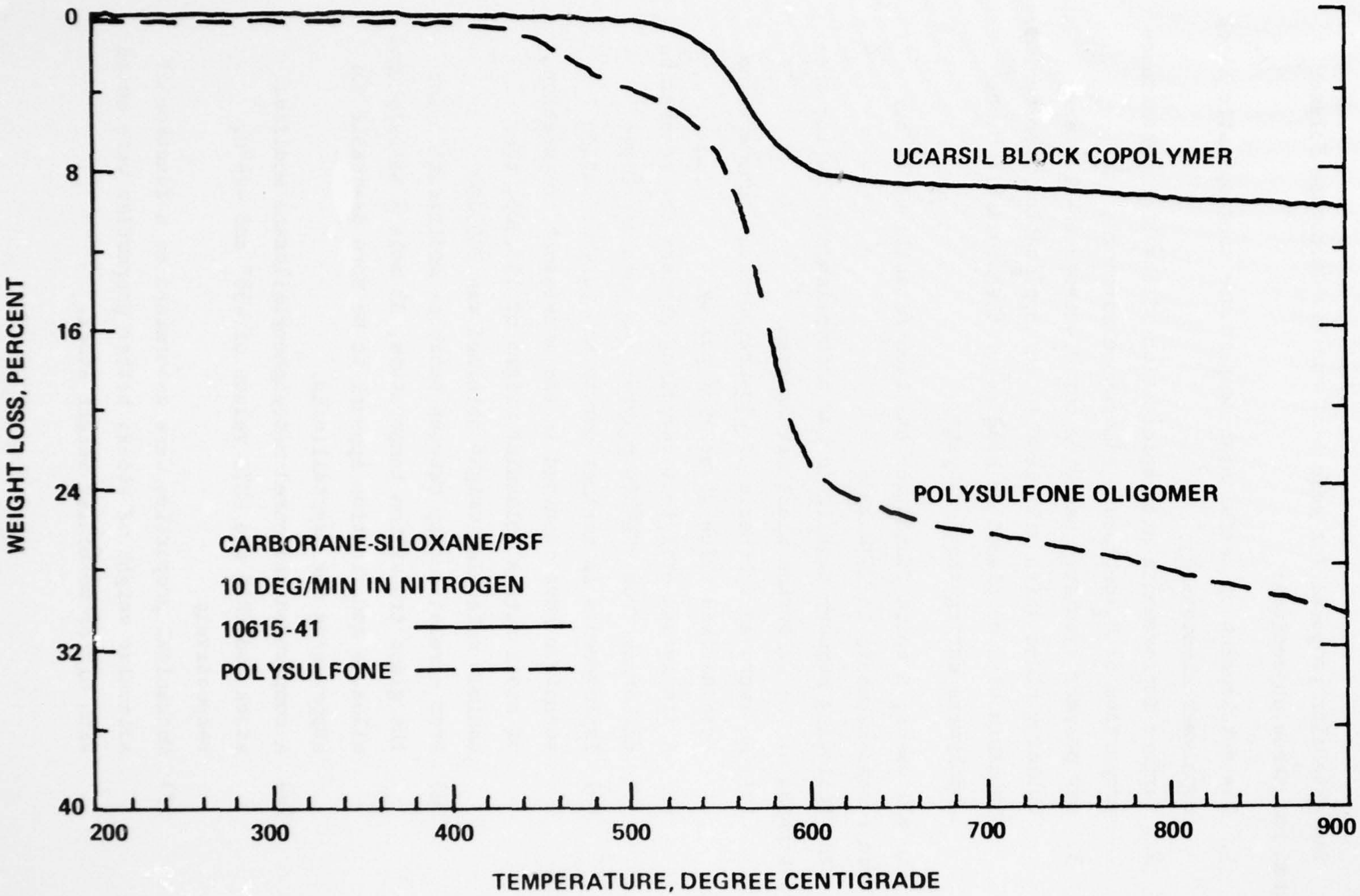


FIGURE 23. THERMOGRAVIMETRIC ANALYSIS OF UCARSIL BLOCK COPOLYMER (10615-41)

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THE PREPARATION AND PROPERTIES OF D2-CARBORANE-SILOXANES.(U)
JUL 75   E N PETERS, C D BEARD, J J BOHAN   N00014-72-C-0277
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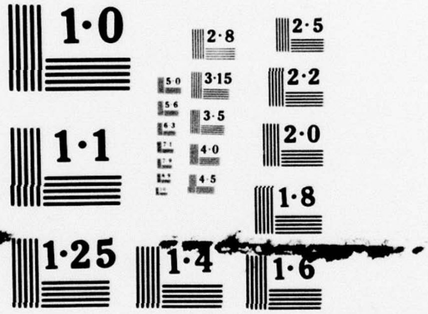

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MICROCOPY RESOLUTION TEST CHART

6.0 SUMMARY

The extension proposal for year 5 of our New Carborane Polymer Program has three objectives:

1. The development of useful high temperature thermoplastic block copolymer elastomers;
2. further improvements and exploitation of the high performance properties of D_2-carborane-siloxane elastomers; and
3. new polymer chemistry based on our D_2-carborane-siloxane building block which will lead to new application opportunities. Emphasis will be placed on studies of thermoplastic block copolymers during the next year.

In all cases, a solid foundation has been established by our research accomplishments in 1974-1975.

The following summary highlights our accomplishments during the current phase of the Carborane Elastomer Program:

(a) An improved synthesis of bis-ureidosilane monomers has been devised which gives >98% purity.

(b) A simple and efficient recycling process for recovering carborane from UCARSIL polymer has been developed.

(c) Improvements in monomer purity and polymerization technique have resulted in the consistent preparation of stock with a molecular weight of 150,000; the maximum molecular weight obtained was 280,000

(d) From a relationship between backbone modification and the glass transition temperature, 33 mole % methylphenylsiloxane modification appears to be more desirable for suppressing the crystallinity.

(e) A compounded and cured methylphenylsiloxane modified stock had TR10 and TR70 values of -38° and -24°C, respectively.

(f) Mechanical properties were determined as a function of molecular weight of stock; better properties were noted with higher molecular weight stock.

(g) From a study of extending fillers, it was shown that the amount of stock needed in our formulations could be lowered.

(h) The use of finely dispersed ferric oxide was shown to be more efficient as an antioxidant than powdered ferric oxide.

(i) The effect of peroxide level on properties was evaluated and 1.5 phr peroxide appeared to be optimal.

(j) D_2-carborane-methyltrifluoropropylsiloxane was shown to have improved solvent resistance.

(k) Block copolymers were made consisting of a UCARSIL soft-block and a polysulfone hard block; this work demonstrated the feasibility of preparing block copolymers utilizing the UCC polymerization process.

(l) Utilizing data from optimization studies conducted in the past two years, we have achieved marked improvements in performance through formulation and vulcanization changes. These results have facilitated our external evaluation program.

Future work will be directed toward the preparation and characterization of new thermoplastic block copolymer elastomers prepared from UCARSIL soft blocks. Larger quantities of high molecular weight stock will also be prepared to support actual evaluations in O-ring, gasket, and sealant applications.

7.0 EXPERIMENTAL SECTION

General

A. Purification of Solvents

Diethyl ether, tetrahydrofuran, heptane, pentane, and benzene were all freshly distilled from sodium-benzophenone ketyl under nitrogen. Pyrrolidine was refluxed over potassium hydroxide for 12 hours and distilled under nitrogen, bp 87-88°. Dichlorodimethylsilane was distilled through a two foot Vigreaux column under nitrogen, bp 70-71°. Phenyl isocyanate was distilled through a two foot Vigreaux column, bp 79-80° (39 mm).

B. Inert Atmosphere Techniques

All glassware was dried in an oven at 140° for at least 12 hours and assembled while warm under nitrogen. All manipulations involving air sensitive materials were carried out using either conventional Schlenk techniques[22] or in a Dry Box. Thus, all apparatus was subjected to several purge and evacuation cycles using nitrogen or argon. Syringe techniques were used to transfer solutions of butyl lithium in hexane. Melting points were determined in capillaries sealed under argon and are uncorrected.

1,2-*bis*(Chlorodimethylsilyl)-*o*-carborane - A 5,000 ml three-necked flask was equipped with mechanical stirring, a reflux condenser, nitrogen inlet, and an addition funnel. *o*-Carborane (200g, 1.39 mol) and 1,500 ml of anhydrous ether were placed in the reaction vessel. The reaction mixture was cooled in an ice bath and a solution of butyl lithium was added dropwise over a period of two hours. After completion of the addition, the cooling bath was removed and the reaction mixture was stirred for 16 hours at room temperature. The insoluble dilithium salt separated from the solution.

The reaction mixture was cooled in a dry ice-acetone bath and a solution of dichlorodimethylsilane (2.919 mol, 377g, 355 ml) in 250 ml of ether was added rapidly (five minutes). There was little detectable exotherm. The reaction mixture was stirred at -78° for three hours and then at 0° for an additional three hours. The cooling bath was removed and the reaction mixture was stirred at room temperature for 18 hours.

The solution was filtered under nitrogen through a fritted filter covered with glass wool to prevent clogging. The filter cake was washed with four 250 ml portions of anhydrous ether.

Most of the solvent was removed by distillation under nitrogen at atmospheric pressure. The crude product was dried in vacuo and recrystallized from heptane. The recrystallized product (pale yellow) was further purified by sublimation (bath temperature 125°) giving 402g (88%) of bis-(chlorodimethylsilyl)-o-carborane, mp 112-114° [lit[23] mp 112.5-113.5°]: nmr (CCl_4) δ 0.75 ppm (s).

bis(Chlorodimethylsilyl)-m-carborane - A modification of the procedure reported by Heying and Papetti was used.[1] bis(Chlorodimethylsilyl)-o-carborane (402g, 1.22 mol) was divided into equal portions in the Dry Box and placed in three 250 ml modified Claisen flasks. The compound was heated at the reflux under nitrogen for 20 hours using a heating mantle. After cooling to room temperature, the material did not solidify. Nmr indicated that isomerization was complete. The singlets at 0.75 ppm (ortho) and 0.52 ppm (meta) were used to monitor the progress of the isomerization reaction.

The crude product was distilled directly from the Claisen flasks giving 362g (90%) of bis(chlorodimethylsilyl)-m-carborane, bp 99-101° (.05 mm) [lit[24] bp 102-104° (0.1 mm)]; nmr (ccl_4) δ 0.52 ppm (s).

1,7-bis(Hydroxydimethylsilyl)-m-carborane - A 5,000 ml three-necked flask was equipped with mechanical stirring, thermometer, and a pressure equalized addition funnel (with side-arm closed). bis(Chlorodimethylsilyl)-m-carborane (360g, 1.094 mol) was placed in the addition funnel under nitrogen and added dropwise over a period of two hours to 3,000 ml of water cooled in an ice bath (0-5°). After completion of addition, the reaction mixture was stirred for an additional hour. The aqueous layer was extracted with three 400 ml portions of ether. The ether layer was washed with saturated sodium chloride solution, dried over $MgSO_4$, and filtered. The solvent was evaporated giving the product as a colorless oil which solidified upon standing.

The crude disilanol was recrystallized from heptane giving 272g (85%) of bis(hydroxydimethylsilyl)-m-carborane, mp 98.5-99.5° [lit[25] mp 98-99.5°].

bis(N-Methyl-p-toluenesulfonamido)dimethylsilane - A three-necked 1,000 ml flask was equipped with mechanical stirring, a reflux condenser, nitrogen inlet, and a pressure equalizing addition funnel. N-Methyl-p-toluenesulfonamide (74g, .4 mol) and 400 ml of benzene were placed in the reaction vessel. A solution of butyl lithium in hexane (2.4 M) (166 ml, 0.4 mol) was added dropwise with stirring and cooling in an ice bath. During the course of addition, the lithium salt of the sulfonamide precipitated out and formed a thick slurry. Stirring became difficult and tetrahydrofuran (300 ml) was added. The reaction mixture was then stirred for 12 hours at room temperature.

A solution of dichlorodimethylsilane (25.8g, 0.2 mol) in tetrahydrofuran (100 ml) was added dropwise with cooling in an ice bath. After completion of addition, the cooling bath was removed and the reaction mixture was stirred at room temperature for three hours. After filtration under nitrogen, the solvents were removed *in vacuo*. The crude solid was recrystallized several times from heptane, giving 25g of the product, mp 158-162°. The nmr and ir spectra were consistent with the structure.

Cleavage of Silylated Carboranes - The silylated carborane polymer (Dexsil 202, 10g) was dissolved in 100 ml of tetrahydrofuran in a 500 ml Erlenmeyer flask. A solution of potassium fluoride ($KF \cdot 2H_2O$, 1g, 10% by weight) in 50 ml of water was added in a single portion. With magnetic stirring and cooling in an ice bath, one drop of a phase transfer catalyst (Adogen 464) was added. When larger quantities of material were employed, an exothermic reaction was observed when the phase transfer catalyst was added. The cooling bath was removed and the two-phase reaction mixture was stirred for 16 hours at room temperature. The layers were separated and the organic layer was washed with saturated sodium chloride solution, dried over $MgSO_4$, and filtered. Evaporation of solvent gave a semi-solid, viscous residue. Sublimation *in vacuo* (.05 mm, bath temperature 85°) gave the solid m-carborane (2.79g, 93%). The residue (not identified) appeared to be a non-boron containing silicone polymer. The sublimed carborane contained small quantities of volatile silicone compounds (presumably cyclic trimers). These impurities were efficiently removed by recrystallization from heptane.

The results of experiments using a variety of silylated carboranes and nucleophiles are tabulated in Table 4.

bis(Pyrrolidinyl)dimethylsilane - A three-necked 2,000 ml flask was equipped with a mechanical stirrer, reflux condenser, nitrogen inlet, and an addition funnel. Dichlorodimethylsilane (129g, 1 mol) and heptane (200 ml) were placed in the reaction vessel. With stirring and cooling in an ice bath, pyrrolidine (284.5g, 4 mol) was added dropwise over a period of two hours. The reaction was slightly exothermic and solid amine hydrochloride began to separate immediately.

After completion of the addition, the cooling bath was removed and the reaction mixture was stirred at room temperature for 12 hours. The solid was removed by filtration under nitrogen and washed with three 50 ml portions of heptane. The solvent was removed by distillation through a 12 inch Vigreaux column at atmospheric pressure under nitrogen. Distillation of the residue gave 174g (87%) of bis(pyrrolidinyl)dimethylsilane, bp 59-60° (.025 mm).

A variety of bis-aminosilanes were prepared using this general method (Table 1).

bis(N-Phenyl-N'-pyrrolidinyl)dimethylsilane - A 2,000 ml three-necked flask was equipped with magnetic stirring, nitrogen inlet, and an addition funnel. bis(Pyrrolidinyl)dimethylsilane (100g, 0.5 mol) and 400 ml of anhydrous ether were placed in the flask. The reaction mixture was cooled to 0-5° in an ice bath. Phenyl isocyanate (119g, 1 mol) was transferred to the addition funnel by syringe and added dropwise over a period of one hour. The solid product slowly separated during the addition. Stirring was continued for one hour after completion of addition and then stopped to allow the solid product to settle out. The ether was decanted under nitrogen and replaced by 400 ml of pentane. After stirring for 15 minutes the pentane layer was decanted. This procedure was repeated with two additional 400 ml portions of pentane. Drying in vacuo gave the product, 199g (91%), mp 124-125°.

Several bis-ureidosilanes were prepared using this general method (Table 2).

General Procedure for the Preparation of Carborane-Siloxane Stock

A mixture of 19.88g (45.54 mmol.) of bis(N-phenyl-N'-tetramethyleneureido)-dimethylsilane, 14.77g (26.34 mmol.) of bis-(N-phenyl-N'-tetramethyleneureido)-diphenylsilane, and 1.455 (3.24 mmol.) of bis(N-phenyl-N'-tetramethyleneureido)-methylvinylsilane in 100 ml of dry chlorobenzene was added dropwise by syringe during 30 minutes to 23.09g (78.93 mmol.) of bis(hydroxydimethylsilyl)-m-carborane to which 10 ml of dry chlorobenzene was added just prior to addition of the silyl bis ureas solution. The m-carborane disilanol which was in a 250 ml three-necked round bottom flask equipped with a mechanical stirrer and two no-air stoppers, was cooled at -10 to 0°C (methanol-ice) under nitrogen during the addition of the silyl bis urea solution.

The mixture was stirred moderately for 15 minutes at -10 to 0°C then allowed to warm slowly to room temperature. After stirring under nitrogen for 90 minutes, the reaction mixture was stirred overnight.

A solution of .600 mg (1.37 mmol.) of bis(N-phenyl-N'-tetramethyleneureido)-dimethylsilane in 5 ml of dry chlorobenzene was added to the reaction mixture (at ~50°C) slowly and continuously over a four-hour period by the use of a syringe pump. After completion of addition, the mixture was stirred for two hours. Similarly, the stoichiometry was further adjusted with carborane disilanol.

The reaction mixture was filtered and the filtrate was coagulated in 10 parts methanol. The amorphous, white stock was then washed with 3 x 10 ml portions of methanol. The material was dried at 150-180°C (1-2 mm) for five hours but still contained solvent. Further drying for two hours at 105°C (30 mm, then .5 mm), one hour at 125°C (30 mm, then .5 mm), one hour at 135°C (30 mm, then .5 mm), and one hour at 145°C (30 mm, then .5 mm) resulted in more solvent loss. NOTE: The higher the phenyl content of the stock, the more amorphous it becomes, retaining solvent more strongly; solvent may interfere in the curing process.

After drying 28.09g (91.2%) of m-carborane-dimethyl/diphenylsiloxane was obtained; nmr analysis of the stock revealed approximately 17 weight percent of diphenyl silyl moieties.

Determination of Mechanical Properties

Specimens were cut from molded plaques using a razor blade and metal straight edge. The dimensions of a strip specimen were 3/16" wide x 2" long. Thicknesses vary from 5 mils to 25 mils.

The mounting of the specimen for testing involves clamping one end of the specimen in the top stationary jaw of an Instron testing machine. The other end of the specimen is clamped in the bottom jaw of the movable crosshead. The distance (gage length) between the jaws is one inch. The jaws move apart at an initial speed of 0.2"/min to 0.01" (1%) elongation of the specimen; the modulus is obtained at this point. Without stopping the crosshead, the downward speed of the crosshead is increased to 2"/min until the specimen breaks; this second phase of the test (stress-strain curve) affords tensile strength and elongation at break data. The stress is automatically plotted against strain (elongation) on the Instron recorder.

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9.0 ACKNOWLEDGEMENTS

The authors wish to acknowledge valuable contributions by Mr. E. R. Wagner in the areas of filler/resin interaction and general elastomer characterization. Productive discussions with Dr. L. M. Robeson are also acknowledged. Mr. A. W. Bedwin determined the relative viscosities of the stocks; Dr. F. D. Osterholtz and Mr. P. F. D'Angelo carried out the surface fluorination.