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Thermally Stable Elastomers: A Review

by
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OCTOBER 1983

**NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555**



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FOREWORD

This review of high-temperature elastomers was performed during fiscal year 1981 and supported by Naval Weapons Center discretionary funds. The treatment of the subject matter is general, but has a specific application in guiding the search for high-temperature elastomeric materials for missile materials such as rocket and ramjet combustion chamber thermal insulation.

This report is released at the working level. Because of the continuing nature of the research, it is possible that the results may be further extended.

This report has been reviewed for technical accuracy by Dr. James C. Baldwin.

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31 October 1983

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(U) A literature review of high-temperature elastomers is presented. Among the types covered are fluorocarbon elastomers, polyorganophosphazenes, organic heterocyclic elastomers, silicone elastomers, and various types of silicone block copolymers.

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SUMMARY

Discussed in this review is the state-of-the-art of elastomers capable of withstanding elevated temperatures. Among the types considered are fluorocarbon elastomers; polyorganophosphazenes; organic heterocyclic elastomers; the silicone elastomers, including polydimethylsiloxane and polymethylphenylsiloxane and various additives that impart thermal stability to these polysiloxanes; and, finally, various types of siloxane block copolymers.

A substantial discussion is devoted to the DEXSIL family of elastomers. These elastomers are polydimethylsiloxanes with *m*-decarborane units in the polymer chain. Other types of blocks that have been added to the silicone elastomer chain are also discussed. These block units include a variety of aromatic and aliphatic units that have been used.

The most promising area for further research in thermally stable elastomers is that of siloxane block copolymers. Since silicone elastomers (e.g., polydimethylsiloxane) tend to degrade to cyclic trimers and tetramers at elevated temperatures because of thermodynamic ring-chain equilibrium, this equilibrium is disrupted if a bulky unit is put into the polymer chain at intervals of three to five dimethylsiloxane units.

INTRODUCTION

There is a continuing need for elastomers capable of withstanding elevated temperatures. Within the defense industry, specific needs are associated with aircraft fuel tank sealants and elastomeric components such as O-rings and gaskets in aircraft and missile structures and engines. In the case of ramjet combustor insulation, there is a need for elastomers capable of withstanding the elevated temperatures associated with aerodynamic heating. For example, the silicone-based elastomeric insulation, DC 93-104, is the material currently used for combustor case thermal protection of airbreathing propulsion systems; no backup material is available. The material is suitable for present-day missions involving hydrocarbon fuels, especially if tactical diameters (less than or equal to 9 inches) are anticipated. However, the Air Force's advanced strategic air-launched missile (ASALM) programs indicate that the performance limitations of this insulator are being reached. Hence, the key to development of a second-generation ramjet combustor insulation depends upon the availability of elastomers capable of withstanding higher temperatures.

Another example is in geothermal applications. There is a need for elastomeric components capable of withstanding the high temperatures associated with geothermal steam.

This review includes a discussion on the current state-of-the-art regarding elastomers capable of withstanding elevated temperatures. The emphasis in this report is on silicon-based elastomers, although a discussion of fluorocarbon and polyorganophosphazene elastomers is included. The definition of thermal stability is presented, followed by a discussion of the thermal stability of commercially available elastomers. Then discussed is silicone elastomer science, particularly in regard to the thermal decomposition and use of additives to increase thermal stability. The remainder of this report then deals with siloxane block copolymers.

An elastomer is a polymer with certain well-defined properties. A polymer is a substance comprising many structural units connected in virtually any conceivable pattern. In the simplest of all polymers, the linear polymer, the structural units are connected linearly to one another (Ref. 1, p. 29).^{*} An elastomer is distinguished from other polymers by two characteristics: (1) Elastomers are capable of sustaining large deformations without rupture, where deformations of five to ten times that of the unstretched length are commonplace. (2) Elastomers are capable of recovering spontaneously to their original dimensions after removal of stress. To satisfy these conditions, an elastomeric polymer consists of long polymer chains connected to one another by crosslinkages, where there are a hundred or more single bonds between points of crosslinkage. In addition, an elastomer must neither be crystalline (or very much so) nor be in the glassy state; i.e., the glass transition temperature must be lower than the elastomer temperature (Ref. 1, pp. 432-4). Substances defined as elastomers in this report are those that are elastomers at ambient temperatures.

The thermal stability of an elastomer is the temperature of incipient chemical alteration of the elastomer, such that the mechanical properties have deteriorated to the point where the elastomer is no longer useful (Ref. 2, pp. 33-34). Unfortunately, this information is seldom presented in the literature in sufficient detail.³

The most frequently used method of determining thermal stability, thermogravimetric analysis (TGA), is done in one of two ways. Either way involves measuring the weight of sample. Dynamic TGA measures the weight of sample as it is being heated, so that a curve of sample weight (ordinarily expressed as weight-percent [wt%]) versus temperature is obtained. Isothermal TGA measures sample weight (ordinarily as wt%) versus time, for a constant temperature. TGA, the most commonly published thermal stability parameter, measures the amount of volatile substances leaving the decomposing polymer; it does not provide a measure of either chain-breaking or crosslinking, parameters of important in elastomer science.

Differential thermal analysis (DTA) measures the difference in temperature between a sample and a reference material as both are heated. Differential scanning calorimetry (DSC) measures heat flow, either into or out of a sample, as the sample is being heated. These

* The list of references is presented at the end of this report

methods are useful in determining glass transition temperature and temperatures of either exothermic or endothermic decomposition.

Thermomechanical analysis (TMA) is a procedure whereby a weighted, pointed rod is put to a polymer surface; as it sinks into the polymer, its position is determined electrically. TMA can be run either isothermally versus time or, more frequently, versus temperature, as the polymer sample is being heated. TMA is essentially a dynamic measure of polymer hardness, in turn a measure of crosslink density.

Torsional braid analysis (TBA) is a technique whereby a polymer, either in a melt or in solution, saturates a fiber braid. A weight is attached to the end of the braid, and the weight is rotated from the rest position. The weight slowly rotates back and forth, and information is obtained from this torsional rotation. Torsional damping versus temperature is obtained, along with complex modulus and mechanical loss information, parameters related to the crosslink density.⁴

Stress relaxation is a technique whereby an elastomer is stretched and held at an elevated temperature. Measured is the stress (at constant elongation) versus time. From this information, the change of crosslink density versus time is estimated.

THERMAL STABILITY OF CONVENTIONAL ELASTOMERS

With the exception of the silicone and fluorinated elastomers, the thermal stability of conventional elastomers is generally less than 200°C. The tensile strength versus temperature for several elastomers (Ref. 2, p. 29) shows that only silicone rubber retains appreciable tensile strength at temperatures above 250°C, compared to the following rubbers: butyl, natural, Hypalon, SBR, nitrile, polyacrylate, or neoprene. The prolonged working temperature for a number of elastomers indicated (Ref. 2, p. 55) the following temperatures: silicone, 180°C; fluorinated rubber, 170°C; polyurethanes, 130°C; and organic rubber, 90°C. The limited working temperatures for a number of elastomers, for 200 hours exposure, are: silicone, 200-280°C and fluorinated elastomers, 200-260°C. The TGA-derived temperature for a weight loss of 1% per minute was presented³ for the following elastomers: polybutadiene, 401°C; polyethylene oxide, 351°C; polyisobutylene, 338°C; natural rubber, 331°C; and polypropylene oxide, 294°C. Although the TGA decomposition temperature for a number of these polymers may be on the order of 400°C, in actual fact the polymer may have substantially degraded (by chain-scission, for example) when that temperature is reached.

FLUOROCARBON ELASTOMERS

Fluorocarbon elastomers are more thermally stable than their hydrocarbon analogs. TGA measurements for a variety of fluorinated polymers show fairly high thermal decomposition temperatures, to 400°C (Ref. 2, pp. 79-81). However, these data must be put into perspective. For example, for the copolymer of perfluoropropylene and vinylidene fluoride (VITON B), the working temperature ranges to 315°C; the relationship between

temperature and hours of elasticity retention (Ref. 2, p. 78) is: 200°C, 2400 hours and 315°C, 24 hours.

KALREZ, the most thermally stable commercially available fluoroelastomer, is a copolymer of approximately 25% perfluoromethylvinyl ether with tetrafluoroethylene, with a continuous service temperature above 260°C.⁵ The procedures for preparation and curing have been published.⁶⁻⁸ From the author's experience, KALREZ, from du Pont, is rather expensive (about \$1000/lb as finished parts), but its performance may well make the cost worthwhile.

Fluorocarbon and fluorocarbon-ether-linked polyheterocyclic elastomers with fairly high heat resistance have been prepared.⁹ The polymer decomposition temperature, PDT (i.e., the TGA inflection temperature), for fluorocarbon-linked s-triazine elastomers and the preparation of these elastomers have been published.¹⁰ These elastomers have a PDT of 351°C, with a tensile strength of 85 kg/cm² and an elongation of 350%.¹¹ For a number of bibenzoxazole elastomers with fluorocarbon or fluorocarbon ether linkage, the PDTs were indicated to range between 400 and 500°C (Ref. 12, pp. 105-7, 144); the preparation of these elastomers has been described by Evers.¹³⁻¹⁹

POLYORGANOPHOSPHAZENES

Trimeric phosphonitrilic chloride can be polymerized at temperatures above 250°C to form an elastomer stable to 350°C. This "inorganic rubber," however, hydrolyzes readily to ammonium chloride and phosphoric acid.^{3,20} As prepared, poly(phosphonitrilic chloride) is elastomeric and also crosslinked; it would be very useful except for its ready hydrolysis with atmospheric moisture.²⁰ To make a useful substance, the alkoxy or aryloxy has been substituted for the chlorine. To produce elastomeric materials, mixed alkoxy- and aryloxy-units have been used. A number of polymers have been made, and the properties of some of them have been published.²¹

One of the polymers that has received substantial attention is the trifluoroethoxy derivative.²⁰ Films of polybis(trifluoroethoxy)phosphazene are unaffected by moisture, glacial acetic acid, pyridine, and concentrated caustic solution (Ref. 12, pp. 199-219). The mechanical properties of the elastomer show a yield strength of 1220 psi and breaking elongation of 130% (Ref. 12, p. 211). The TGA shows an inflection around 330°C,²² and the molecular weight distribution versus temperature for a 30-minute exposure shows little degradation at 275°C but substantial degradation at 300°C.

Polymer crystallinity results from the regular arrangement of substituent groups along the polymer chain; the absence of crystallinity is often associated with elastomeric properties. Hence, elastomeric properties are more likely if there is a random attachment of two or more different groups on the chain.²⁰ For example, the mixed trifluoroethoxy heptafluorobutoxy-substituted phosphazene elastomer has been prepared;²⁰ this elastomer reportedly remained unchanged upon prolonged contact with boiling water, common organic solvents, and concentrated potassium hydroxide (Ref. 12, pp. 199-219).

The crosslinking of phosphonitrilic elastomers can be effected by conventional curing agents, such as organic peroxides or sulfur. Crosslinking can also be accomplished by the disodium salt of a diol.²¹

In general, isothermal aging of polyorganophosphazenes had resulted in greater degradation than desired for thermally stable elastomers (Ref. 12, pp. 199-219). The elastomers underwent rapid degradation at first, followed by a gradual decrease in molecular weight. The degradation mechanism was found to be consistent with initial random chain scission at weak sites along the polymer, followed by depolymerization to cyclic oligomers. The weak sites postulated include -P-OH, -P-Cl, and other sites. The Firestone Tire and Rubber Co. has tried deactivating weak sites by the addition of stabilizers. In one example, Firestone used bis(8-oxyquinoline)zinc with poly(fluoroalkoxyphosphazene) elastomer and found that the stabilizer definitely aids in increasing thermal resistance. Since several substituted cyclotriphosphazenes had decomposition temperatures above 300°C, there is the potential for equally high temperature resistance of the polymer. Further effort is required toward eliminating or deactivating the weak links of the polymer. In addition, a possible approach may be to introduce blocks in the polymer chain, analogous to the method used with the silicones (to be discussed later in this report (Ref. 12, pp. 199-219)). There is a substantial potential for the polyorganophosphazenes. A pioneer in this science, H. R. Allcock, has written that this science has reached the state of development that existed in silicone technology in the early 1950s, and that the way is now open for broad development of the technology.²¹

HETEROCYCLIC ELASTOMERS

Since the 1960s an enormous amount of research has been devoted to preparing and characterizing polymers that are stable at high temperatures. These polymers are generally heterocyclic materials, including polyimides, polyphenylquinoxalines, and a wide variety of others. A number of excellent reviews are available.^{2,3,9} These polymers, while very stable thermally, almost invariably are quite hard, with breaking elongations of only a few percent. Nevertheless, there are a few examples in the literature of organic polyheterocycles that are reported to be somewhat elastomeric.

Korshak reported a plasticized poly-p-xylylene having 600% elongation (Ref. 2, p. 60). This polymer reportedly melts at 410-429°C, and decomposes above that temperature (Ref. 2, p. 89). He and co-workers also patented the preparation of poly(phenylquinoxaline imides),²³ the films of which were elastomeric. In one example in his patent, he described the reaction of naphthalene tetracarboxylic dianhydride with a bis(aminophenylquinoxaline) in a phenol/nitrobenzene solution to make a polymer with a tensile strength of 1800 kg/cm², an elongation of 120%, and elasticity retention after 1 hour at 400°C.

Yoda et al. patented an intriguing series of thermally stable elastomeric spirocyclic polyimides.²⁴ An example was the preparation of a polymer by a two-stage heating process. In this case, a mixture of 3,3'-diamino-4,4'-biphenol and trimellitic anhydride chloride was reacted in solution at subambient temperatures. The mixture was warmed to room temperature; pyromellitic dianhydride and bis(p-aminophenyl)methane were added; and the

mixture was stirred at room temperature, then heated for various periods of time at 80, 100, 185, and finally 378°C to yield a poly(imide benzoxazole) film with an elongation of 96%.

Jones and co-workers at TRW Inc. described the preparation and properties of flexible polyimides to be used as aircraft fuel tank sealants.²⁵⁻²⁷ Their approach was to copolymerize ethylene aniline and a polyethyleneoxide diamine (of 1400 molecular weight), with the dianhydride bis(3,4-dicarboxyphenoxyphenyl)sulfone dianhydride. By using a weight ratio of 75:25 of ethylene diamine with the polyethyleneoxide diamine in the copolymerization, they were able to optimize on tensile property (tensile strength, 4640 psi; 65% elongation) and thermal stability (around 300°C).

SILICONE ELASTOMERS

GENERAL CONSIDERATIONS

In the later 1930s the need in industry for polymers more heat resistant than organic polymers then available provided the incentive for exploring the chemistry of the silicones.²⁸ Since then, silicone elastomers have been widely used in a number of industries. The word "silicone" was originally applied to diorganosiloxanes and derived from the formal analogy between the empirical formula of diorganosiloxane and an organic ketone. However, unlike the organic ketones, the diorganosiloxanes are polymeric, cyclic, or linear molecules.²⁹

Silicone polymers, including elastomers, are prepared by a two-step process consisting of (1) the hydrolysis of an organochlorosilane (e.g., dichlorodimethylsilane) to a mixture of cyclic trimers, tetramers, and higher cyclic and linear polymers, and (2) the ionically catalyzed polymerization of these oligomers to produce the polymer. In the process, ends of the polydimethylsiloxane are capped with a mono-silanol. Molecular weights ranging from 1,000 to 1,000,000 for the polymer have been made. Although the organochlorosilanes were first produced by a Grignard method, large-scale industrial production of the silicones became feasible only when the process for production of the organochlorosilanes by the direct reaction of organic halides with silicone (the Rochow process) was developed.³⁰

Polmanteer reported that the continuous exposure temperature versus service life of silicone elastomers ranges from 15,000 hours at 148°C to 15-30 minutes at 371°C.³⁰ Some of the uses for high-temperature silicone elastomers are gaskets for oven and autoclave doors and processing of hot glassware and metals.

This review of silicone elastomers deals with thermal stability in an inert atmosphere, in air (thermo-oxidative stability), or in the presence of water (hydrolytic stability). Current thinking regarding the thermal decomposition of silicone elastomers and the effect of additives for control of this decomposition is also covered.

THERMAL DECOMPOSITION

Andrianov has stated that many of the properties in siloxane elastomers are the result of molecular structure (Ref. 31, p. 272). For example, the polydimethylsiloxane

molecules are in a spiral form with six to eight links in the spiral. At high temperatures, warping of sections of chain links has resulted in closure of the chains into rings, where chain links in the spiral are close together. If there were phenyl or other groups on the silicone atom, there would be a decreased tendency toward spiral structure, leading to stabilization of the polymer. Baney indicated in a review that high-temperature degradation consists of siloxane rearrangements and ring-chain equilibrium.³² The silicone-carbon bond can withstand 600°C, while 250-350°C is the temperature limit within which silicon-oxygen bond rearrangements occur. The equilibrium between cyclic and polymer structure is shifted in favor of cyclic components at elevated temperatures.

Polymethylsiloxanes undergo thermal rearrangement with the rupture of the siloxane chain to form products which are predominantly cyclic siloxanes of low molecular weight.³³⁻³⁵ In addition to Andrianov's concept that ring formation is produced by elements of the spiral molecule touching, there are theories that the end-groups play an important role in the thermal decomposition.³³ Silicone elastomers are hydroxyl terminated if water is used for chain-stopping during polymerization. However, the decomposition temperature is increased if other groups are substituted for hydroxyl. For example, in the case of polydimethylsiloxane, replacing the hydroxyl end-groups with methyl or other groups decreases the rate of decomposition.³³⁻³⁵ for polymethylphenylsiloxanes, replacing hydroxyl with other end-groups substantially reduces the decomposition rate.^{39,40} Triphenylsilyl end-groups are substantially more effective than trimethylsilyl end-groups.⁴⁰

The procedure for making high molecular weight polydimethylsiloxane is the ring-opening polymerization of cyclic intermediates.³⁰ This reaction is catalyzed by strong bases (alkali metal hydroxides, for example); octamethylcyclotetrasiloxane is converted to high molecular weight polymer after heating for 2 hours at 140°C in the presence of 0.01% KOH. However, the catalyst, which remains in the polymer, causes depolymerization at higher temperatures; in the presence of 0.01% KOH, the polymer loses 99% of its weight at 250°C in 20 hours (Ref. 31, p. 279). There are other literature examples of silicone degradation in the presence of small amounts of base. Polydimethylsiloxane samples containing 0.1% KOH degrade rapidly at <300°C;⁴¹ when washed once, the polymer degrades between 300 and 400°C; and, when washed several times, it shows weight losses between 400 and 500°C. Grassie et al. found essentially the same results with poly(dimethyl/diphenyl)siloxane;⁴² they also reported that polydimethylsiloxane with 5% KOH began degradation slightly above 100°C.³⁷ Baney discussed the concept of "active sites," which cause depolymerization and which are supposedly the silanolate sites used in the polymerization.³²

One method of dealing with these "active sites" is to neutralize them.³² another way is to carefully wash the polymer, as discussed above. However, yet another method is to use a base which can be completely decomposed by heating. Andrianov discussed (Ref. 31, pp. 278-86) the use of either tetramethylammonium hydroxide or tributylphosphonium hydroxide as catalysts in the preparation of silicone polymer by ring-opening polymerization. He showed by TGA that higher temperatures were required for degradation of the silicone elastomers prepared with these catalysts. In addition to Andrianov, Goldfarb,⁴³ Gol'din et al.,^{44,45} and also Grassie et al.^{37,39,42,46} have used tetramethylammonium hydroxide catalyst to make silicone elastomers by ring-opening polymerization where TGA polymer decomposition temperatures greater than 300°C were reported.

For thermal stabilization in the absence of oxygen, the additives most mentioned in the literature were cerium compounds. Baney stated that cerium salts were effective in stabilizing dimethylsiloxane, but had no effect upon polyphenylmethylsiloxane units.³² The most effective salt was the acetylacetonato cerium complex. The cerium compounds apparently form active sites but react reversibly with anion fragments, thus limiting further degradation.⁴⁷ The thermal degradation of a methylvinylsiloxane rubber at 300-450°C is inhibited by the addition of 3% lanthanum hydroxides;⁴⁸ however, of a number of rare earth oxides tested, cerium oxide, along with ferric oxide, inhibits the degradation at 300 for >36 hours.⁴⁹ Rode et al. reported that tetrabutoxytitanium or zirconium acetylacetonate increases the thermal stability of polydimethylsiloxanes.³⁸

OXIDATIVE DEGRADATION

Oxidative degradation of silicones generally becomes important in the temperature range 250-300°C. In the presence of oxygen, the pendant methyl groups in the siloxane chain are first oxidized to hydroperoxide groups, which then eliminate formaldehyde to leave silanol groups in place of the methyl groups on the chain. At the same time, the volatile cyclosiloxanes are formed by reaction of silanol in or at the ends of the chain, with siloxane bonds in the chain.^{31,32,50} Crosslinking was observed during the degradation process.³⁷ A TGA of polydimethylsiloxane indicated that the initial weight loss, in both air and nitrogen, was around 260°C, but that the sample lost all of its weight by around 600°C in nitrogen and no more than half its weight in air.⁵¹ Sobolevskii reported that polydimethylsiloxane degraded twice as fast in nitrogen as in oxygen and that an alternating arrangement of methyl and phenyl radicals in the polymer has a stabilizing effect on the thermo-oxidative degradation at temperatures greater than 400°C.⁵² The oxidative degradation of silicones has been reviewed by Baney³² and Andrianov (Ref. 31, p. 272).

Since the organic groups attached to silicon are principally involved in the oxidation, the decreasing order of thermal stability was reported⁵⁰ to be phenyl > methyl > ethyl > propyl > vinyl; for example,⁵³ polyphenylmethylsiloxane was found to exhibit higher thermal oxidative stability than polydimethylsiloxane during oxidation at 280-340°C. This was attributed to the higher oxidation stability of phenyl groups in comparison to methyl groups as well as to an inhibiting influence of the phenyl groups on the oxidation of methyl groups, not only because of the electron-withdrawing effect of the phenyl groups, but also because of the interaction with peroxide radicals to form phenolic products.

Considerable research has been devoted to oxidative stabilizers for silicones.³² The effect of fillers is considered first. Williams⁵⁴ reported that, for a polydimethylsiloxane containing vinyl groups, only an ashen residue remains after heating for 3 days at 316°C with no fillers present. However, the use of 5 parts per hundred of gumstock (phr) SAF carbon black and 0.8 phr ditertiary butyl peroxide results in retention of 89 and 60% of the tensile strength after 3 and 7 days aging at 316°C. Under the same conditions, 20 phr ferric oxide produces 68 and 53% tensile strength. Ground quartz did not improve the heat-aging properties; but precipitated silica, incorporated as an additive, resulted in about 30% retention of tensile strength after 3 days aging. Silica is widely used for reinforcement of silicone elastomers.⁵⁰ Skorik reported that finely divided alumina and silica increased the degradation rate of polydimethylsiloxane at temperatures greater than 300°C, but had no

effect at temperatures less than 300°C.⁵⁵ He also reported that calcium, beryllium, and magnesium oxides greatly increased the thermal degradation of that elastomer.

A substantial effort has been devoted to the use of organic materials, including antioxidants, to improve the thermo-oxidative stability of silicone elastomers. Out of a number of organic antioxidants admixed with GE's Versalube F-50, a polydimethylsiloxane containing an occasional phenyl group, Atkins et al. found that the following provided thermo-oxidative stability to 500°C: condensed aromatic ring compounds containing three or more rings, dinaphthalenethiophene, 2,5-diphenyloxazole, N-phenylferrocenecarboxamide, and 4,4'-bis(dimethylamino)benzophenone.³⁴ Others have found that phenyl-alpha-naphthalene causes improvement at 250-300°C. Prober reported the use of amides as heat stabilizers for polydimethylsiloxane prepared by cyclopolymerization of the cyclic tetramer with 0.01% KOH.⁵⁶ This polymer failed after 2 days at 300°C, but survived upon addition of 0.4% of the following amides: adipamide, urea, and diphenyl urea. Harada reported that a polydimethylsiloxane oil (viscosity, 100 centipoise) gelled after 1 hour at 300°C, but when two parts 2,2-diphenyl-1-picrylhydrazyl was added, there was no gelation after heating 24 hours at 300°C.⁵⁷ Austin and Baney reported that a trimethylsiloxy-end-blocked dimethylpoly-siloxane fluid with a viscosity of 6000 cS began to degrade rapidly when heated in air to 320°C; however, upon addition of 5% or 2.5% tetracyanoethylene, the silicone did not begin to decompose until the temperature was raised to 370°C.⁵⁸ Berlin et al. discussed how poly-2-methyl-5-ethynylpyridine (PMEC) improved the thermo-oxidative stability of a polydimethylsiloxane, with or without added silica.⁵⁹ A concentration of 2 phr PMEC resulted in the silicone withstanding 350°C for 3 hours; whereas, without the additive, the silicone elastomer disintegrated. Gilbert and Kantor reported that polydimethylsiloxane, prepared by cyclopolymerization of the tetramer with 0.01% KOH, was destroyed by heating for 2 hours at 325°C.⁶⁰ However, when 0.357% tri-n-butylphosphine oxide was added, the silicone survived with about 60% retention of tensile properties. They found similar results by using diphenylmethylphosphine oxide.

The remainder of this discussion deals with the use of inorganic or organometallic compounds; those of iron and cerium have been found to be the most successful as thermo-oxidative stabilizers for silicone elastomers.

Iron compounds, and in particular ferric compounds, are used widely as stabilizers for silicones. Ferric oxide is perhaps the most commonly used, as it gives minimal inhibition of peroxide during cure and is believed to be more effective than most other antioxidants, either organic or inorganic.⁵⁰ A dimethylsiloxane elastomer with vinyl groups, cured with 2 phr dicumyl peroxide, degraded in 3 days at 316°C, whereas the formulation with 20 phr ferric oxide withstood 7 days at 316°C or 2 hours at 371°C. (The control failed under these conditions.)⁵⁴

A very common form of iron used as antioxidant is the iron salt of carboxylic acids. Baney proposed that the iron may function to oxidize the free radicals generated in the chain oxidation process by either electron or ligand transfer to a carbonium ion, the ion being reduced from ferric to ferrous; he mentions precedents to support his argument.³² Nielsen used ferric octoate to stabilize the thermo-oxidation of silicone oil.⁶¹ Although his postulate is that of Baney for elevated temperatures, he points out that, below 150°C, the ferric octoate actually increases the oxidation rate. He attributes this oxidation of the silicone at lower temperatures to the ferric-ferrous oxidation. Talcott reported that polydimethylsiloxane with

35 phr fume silica, cured with 1.5 parts benzoyl peroxide, when heated to 300°C for 16 hours, became brittle and useless.⁶² The rubber retained its elasticity and usefulness if either 0.12 part ferric octoate or 0.024 part ferric acetate were added to the formulation. Maciejewski stated that when 8 grams of ferric octanoate and 2 grams of diphenylsilanediol were added to 1000 grams of methylsilicone oil (viscosity, 200 centipoise), fast decomposition began at 380°C versus 320°C for unstabilized oil.⁶³ Kishimoto et al. reported that adding 2 phr ferric 2-ethylhexanoate to 100 cS silicone oil resulted, after 48 hours heating at 250°C, in a product viscosity of 13 cS, compared to the control, which gelled after 24 hours heating.⁶⁴ Buehler reported the use of ferric octanoate, along with any one of a number of polycarboxylic acids (0.2% Fe) for stabilizing 20-cS silicone oil.⁶⁵

Ferrocene and its derivatives have been used for thermo-oxidative stabilization of silicones. Tubyanskaya et al. stabilized elastomers, either polydimethylsiloxane or methylphenylsiloxane, with ferrocene, ferrocenedicarboxylic acid, and hexaphenyldisilylferrocene.⁶⁶ They reported that 0.2-0.5% was adequate for stabilization of the polymer at 250°C, whereas around 5% of ferrocene or its derivatives was required for thermo-oxidative deterioration by a factor of 182. Piccoli stabilized a 1000-cS dimethylpolysiloxane fluid, which was trimethylsiloxy end-blocked, with ferrocene: at 250°C, the untreated fluid gelled in 31 hours; with 0.04% ferrocene, the gel time was 115 hours, and with 0.6% ferrocene, the gel time was 2256 hours.⁶⁷ He also reported enhanced thermal stability, with 0.5% ferrocene, of a number of oils and elastomers containing methyl, phenyl, and vinyl groups, at 250°C.

There are a few other examples of silicone elastomer stabilization by iron compounds: finely divided iron,⁶⁸ ferric acetylacetonate,⁶⁹ 0.1% iron carbonyl,⁷⁰ and 0.1-10% (octaphenylporphyrazinato)iron.⁷¹ Berlin et al. added 5 phr iron oxide, in conjunction with 0.5 to 3 phr poly-2-methyl-5-ethynylpyridine, to polydimethylsiloxane and exposed it to 350°C for 3 hours.⁵⁹ The elastomer remained intact; whereas, without the polymer additive, the elastic properties of the silicone were destroyed.

The rare earths, cerium in particular, have been found effective as antioxidants for silicones. For peroxide-cured dimethylsiloxane elastomers containing small amounts of vinyl, cerium oxide and hydroxide have been found effective.^{72,73} Examples were given where the control elastomer disintegrated after 16 hours at 300°C, but remained viable in the presence of 0.05 to 0.4% cerium in the form of oxide or hydroxide. Lagarde et al. reported that the use of combinations of platinum, silica, and cerium hydroxide improved the thermal stability; the oxides were believed to combine with the degradation products to produce the stabilizing effect.⁷⁴

Cerous naphthenate has been used as stabilizer in a peroxide-cured polydimethylsiloxane, which without stabilizer became brittle after heating for 48 hours at 315°C. This elastomer held up satisfactorily when 0.046% cerium, as naphthenate, was added.^{75,76} Koda et al. prepared cerium siloxanoates, which were soluble in silicones, as stabilizers, and claimed that these materials were more effective than the corresponding insoluble cerium compounds.⁷⁷⁻⁷⁹ In their approach, cerous 2-ethylhexanoate was treated with potassium siloxanolate and then added as a 3% adduct to the silicone, thereby stabilizing the silicone to exposure to 300°C.

Other rare earths have also been used as thermo-oxidative stabilizers. A polydimethylsiloxane elastomer containing 35 phr silica and 20 phr diatomaceous earth was

shown to have improved heat stability toward exposure for 16 hours at 300°C, when either 2.54 phr lanthanum oxide or 2.5 phr mischmetall oxide (mischmetall is a mixture of rare earth metals) was added.⁷³ A patent describes a peroxide-cured polydimethylsiloxane containing 45 phr silica that, without stabilizer, became too brittle to test when heat aged 24 hours at 315°C.⁹⁰ Under the same conditions, adding 5 phr red iron oxide to the formulation resulted in an elongation of 190%; adding 0.04 phr mischmetall octoate resulted in 210% elongation; adding 0.062 phr mischmetall chloride resulted in 260% elongation; adding 0.042 phr mischmetall acetate resulted in 110% elongation, and adding 25 phr oxide resulted in 40% elongation. Hence, the octoate or chlorides of mischmetall were found to be quite effective as stabilizers. Berlin et al. reported that a peroxide-cured polydimethylsiloxane which contained 40 phr silica disintegrated during air aging for 3 hours at 350°C.⁵⁹ Adding poly-2-methyl-5-ethynylpyridine (0.5 or 1 phr) along with three parts cerium oxide or 1 phr cerium naphthenate resulted in the silicone elastomer retaining elasticity under the test conditions. The silicone elastomer also withstood the test conditions if, instead of the cerium compounds, ytterbium or lanthanum naphthenates were used.

Cobalt and copper substances have been used as thermo-oxidative stabilizers. Gladyshev et al. used finely divided copper metal for this purpose.⁶⁸ Grinblat et al. reported the stabilization of silicone elastomers with copper salts (including silicates, sulfides, borates, and phosphides).⁸¹ In an example, 1 phr copper metasilicate stabilized a silicone elastomer against 72 hours aging at 300°C. In other work, a polydimethylsiloxane which contained 35 phr fume silica and was peroxide-cured disintegrated after 48 hours at 315°C.^{75,76} The addition of either 0.057 phr cobalt (as octoate) or 0.11 phr copper (as octoate) to this elastomer stabilized the silicone so that it was elastic under the described test conditions. For a similar silicone elastomer, Hill and Richardson reported that the elastomer became brittle after 1 day at 300°C, but retained its elasticity if 0.5 phr copper oxanilide were added to the formulation.⁸² Kolenytsyn et al. stabilized a silicone elastomer with copper methionate and phthalate with respect to aging at 300°C for 24 and 48 hours.⁸³

A number of other substances have been used for stabilization of silicone elastomers. Generally, these elastomers are polydimethylsiloxanes, peroxide-cured, with fume silica added. Laur showed that substituting 1 phr titanium dioxide for the silica resulted in stabilization of the elastomer for 24 hours at 250°C.⁸⁴ In another example, the use of 33% titanium dioxide in the formulation caused a decrease in the oxidative degradation rate, compared with unfilled polymer (at 250-330°C), by a factor of 20 to 30.⁸⁵ When 1.2 phr tetraphenoxytitanium was added to the silicone elastomer, it was able to withstand 24 hours at 316°C, whereas the elastomer crumbled without the additive. Bis(triphenoxytitanium)oxide and tetrakis(p-methylphenoxy)titanium also were effective. Wormuth reported that addition of 0.1-10 phr barium oxide and 1-10 phr ferric oxide, together, stabilized a silicone elastomer to 168 hours at 248°C.⁸⁶ Viksne found that a control silicone elastomer became brittle after 24 hours at 316°C, but that the elastomer retained its elasticity if either 3 phr titanium dioxide, 2 phr ferric oxide, or 2 phr cerium stannate were added.⁸⁷ Finally, Hatanaka et al. reported that a control silicone became brittle after 24 hours at 300°C, but if 0.1 part magnesium ferrite were added, the elastomer retained its elasticity after the test.⁸⁸

HYDROLYTIC STABILITY

The reaction of a siloxane linkage with water results in the cleavage of the siloxane bond to give two silanol groups. The effect of hydrolysis is indistinguishable from siloxane rearrangement, since the effect on the mechanical properties is the same. The rate of hydrolysis is increased by catalysts; thus, it is very important to eliminate catalytic impurities such as acid-forming peroxides from elastomers if contact with water is expected. One method of dealing with hydrolysis is to increase the crosslink density.³⁰

Hydrolysis of the Si-O-Si bond occurs slowly even at room temperature. Silicone elastomers are depolymerized in the presence of water at 120-300°C; in addition, moist air greatly decreases the stability of methylvinylsilicone rubbers at temperatures ranging from 160 to 250°C. Further, siloxane polymers have been hydrolyzed with steam at 200-250°C. It was found that the following catalysts increase the hydrolysis rate of silicones: potassium silanolate, ammonium iodide, sulfuric acid, acetic acid, benzoic acid, hydrochloric acid, phosphoric acid, formamide, ethylene diamine, triethylamine, and quinoline. The following had no effect: ammonium hydroxide, potassium carbonate, and potassium hydride.³² Wormuth reported that 0.1 to 10 parts of barium oxide, with 1 to 10 parts ferric oxide, aided in resisting degradation of peroxide-cured silicone rubbers at elevated temperatures in the presence of moisture.³³

FLUROSILICONE ELASTOMERS

Although the term "fluorosilicone" could conceivably mean any silicone with substituted fluorine, the term has ordinarily been reserved to poly(methyl-3,3,3-trifluoropropylsiloxane). Fluorosilicone elastomers were introduced as a commercial product in 1957. (Another type of siloxane polymer, the hybrid fluorosilicone, which contains a fluorinated segment inserted in the backbone of the polymer chain, is discussed later in this section.) Fluorosilicones are used in aircraft and automobiles as seals, gaskets, and valves because of good fuel and oil resistance combined with thermal stability and low-temperature flexibility.⁵⁰

To prepare fluorosilicones, the monomer, methyltrifluoropropyl-dichlorosilane, is synthesized by the addition of vinyltrifluoromethane to methyl-dichlorosilane.^{89,90} The monomer is then hydrolyzed to the cyclic trisiloxane, which is then cyclopolymerized in the presence of base catalysts at elevated temperatures. Commercial fluorosilicones have a degree of polymerization of around 5000; however, by end-blocked chain termination, fluorosilicone oils and fluids are also produced. The fluorosilicone elastomers are ordinarily vulcanized by peroxide attachment to occasional vinyls incorporated pendant to the polymer chain.

The primary value of fluorosilicones is their resistance to solvents at elevated temperatures. For example, a fluorosilicone with a breaking elongation of 550%, after being aged in JP-4 fuel for 28 days at 260°C, still had 250% elongation. A comparison of a fluorosilicone, which by TGA decomposed 4% at 450°C, with 2,2,2,1-tetrafluoroethylsilicone (8% decomposed at 172°C) and 2,2-difluoroethylsilicone (14% decomposed at 170°C) shows the stability of the trifluoropropyl unit in the fluorosilicone.³ The thermal stability is strongly dependent upon the amount of base present (Ref. 2, p. 42). Some TGA deflection temperatures

are as follow: fluorosilicone with 0.75% KOH, around 150°C; commercial fluorosilicone, around 250°C; and fluorosilicone with KOH very carefully removed, around 400°C. Although the oxidative degradation of fluorosilicone begins around 200°C, metal oxides are found to inhibit oxidation and decomposition of fluorosilicone elastomer in the range of 250-300°C; ferric oxide is regarded as the most effective.⁵⁰

The hybrid fluorosilicones contain fluorinated segments between (trifluoropropyl)methylsilane moieties in the polymer backbone. The fluorinated segment is of the form: -ethylene(group)ethylene-, where the (group) is a fluorocarbon or perfluoroether.⁵⁰ These polymers are elastomeric with good solvent resistance, thermal stability, and, in particular, outstanding reversion resistance, a property particularly important to their use as seals in a hot solvent environment.

An example of a hybrid fluorosilicone preparation follows in which the (group) is perfluoroethylene.⁵⁰ In the first step, 1,2-dibromotetrafluoroethylene is added to ethylene to make 1,6-dibromo-3,3,4,4-tetrafluorohexane. This compound is dehydrobrominated to make 3,3,4,4-tetrafluoro-1,5-hexadiene, which is then added with chloroplatinic acid catalyst to methyltrifluoropropylchlorosilane; this material is then hydrolyzed to the polymer. Other schemes are also employed. This polymer was found to be reasonably stable at 250°C in air or in a sealed glass container. The preparation of hybrid fluorosilicones containing other (group)s has been described.⁹¹ Griffin discussed the thermal stability versus the nature of (group), where (group) is an x-mer of difluoromethylene.⁹² When x = 2, thermal stability is in the range of 270-280°C, but when x = 8 to 10, the thermal stability is in the range 300-310°C.

POLYSILAZANES

Polysilazanes are regarded as analogous to the silicones, except that an NH group replaces the oxygen in the polymer chain. There are a few intriguing literature references regarding thermally stable polysilazanes.

Byrd reported a polymer prepared by the reaction of dichlorodimethylsilane with mixtures of triethylamine and various diamines.⁹³ A very elastic polymer film resulted when the reaction product was cured by heating at 204°C for 2 hours and at 315°C for 1 hour. Xie et al. reported the preparation of a polymer containing a cyclobis(dimethyl)silazane, two diphenylsilanes, and three dimethylsiloxane units in the polymer repeating unit.⁹⁴ The elastomer reportedly withstood 350°C for 24 hours in air.

SILOXANE BLOCK COPOLYMERS

GENERAL DISCUSSION

This section of the report deals with siloxane block copolymer elastomers. These are polysiloxanes with block units in the main-chain for the purpose of enhancing thermal stability. This enhancement of thermal stability is due to the fact that the block units

interfere with the tendency of the polymer to adopt the helical structure characteristic of the polysiloxanes. The disruption of the helical structure inhibits the degradation of the polymer to cyclic units and hence increases thermal stability.

The first series of polymers to be discussed is the DEXSIL series of elastomers. The DEXSIL elastomers are siloxane block copolymers in which the block units consist of dodecacarborane units. The Office of Naval Research supported the study of DEXSIL for 12 years, and scientists at the Olin Matheson Corp. were heavily involved in this effort.⁹⁵

The next group of polymers to be discussed is the silphenylene-siloxane copolymers. These polymers contain phenylene units in the main-chain and are more thermally stable than their silicone analogs. Following this is a discussion of other types of block copolymers that have been prepared.

DEXSIL ELASTOMERS

The DEXSIL family of elastomers refers to block copolymers of siloxane units and block units of bis(dialkyl)silyldodecacarborane, where the alkyl groups are ordinarily methyl. There are several excellent reviews regarding DEXSIL elastomers.^{95,96} In their preparation, the parent carborane is made from the addition of acetylene to decaborane to produce the ortho-carborane; this is converted to the meta-form by thermal rearrangement.⁹⁷ The hydrogen bonded to the carbon is quite acidic; hence, the next step in the preparation is the reaction of butyllithium with the carborane to make the dilithiocarborane. The dilithio compound is then treated with dichlorodimethylsilane to make bis(chlorodimethylsilyl)carborane. The next step is hydrolysis to the corresponding diol, bis(hydroxydimethylsilyl)carborane, for the meta- and para- isomers; an unreactive cyclic compound is formed from the ortho- isomer upon hydrolysis.

The meta-disilanol could not be homopolymerized.^{97,98} However, to make the polymer, the disilanol was co-reacted with the dimethoxy derivative, using ferric chloride as catalyst. The product of this reaction is called DEXSIL 100, based upon the fact that there is one oxygen in the chain for every carborane unit. This polymer, also called D1-carboranesiloxane, is crystalline.⁹⁶

DEXSIL 200, or D2-m-carboranesiloxane, was first prepared by the condensation polymerization of dichlorodimethylsilane with bis(methoxydimethylsilyl)m-carborane, using ferric chloride as catalyst. The ferric chloride, however, induced some crosslinking into the resulting polymer, so that processing of this material was somewhat difficult.^{96,97} Even so, a number of studies were made of this polymer.⁹⁷ The crosslinking reaction catalyzed by ferric chloride was circumvented by the reaction of bis(hydroxydimethylsilyl)m-carborane with dimethylbis(dimethylamino)silane. No crosslinking occurred; however, the polymers were of low molecular weight (around 18,000) due to the dimethylamine-induced cleavage of the carborane-silicon bond (Ref. 12, p. 103). This problem was resolved by the use of silyl urea intermediates such as the bis(N-phenyl-N-tetramethylene ureido)silanes, which react with bis(hydroxydimethylsilyl)carborane to make a by-product urea substance that does not affect the polymer. Thus, carborane-siloxane elastomers with very high molecular weights, in the order of a million, were prepared (see Ref. 12, p. 103, and also Refs. 98 and 99).

DEXSIL elastomers that contain more dimethylsiloxane groups, such as DEXSIL 300, 400, and 500, were made by hydrolytic polycondensation. DEXSIL 300 was made from the monomer, bis(chlorotetramethylsiloxy)carborane, either by hydrolytic condensation or by converting to diol and polymerizing with sulfuric acid catalyst. Another way to make the polymer is the ferric chloride catalyzed copolymerization of bis(methoxydimethylsilyl)carborane with bis(chlorodimethylsilyl)ether. DEXSIL 400 and 500 have been made by similar methods (see Ref. 12, p. 105, and also Refs. 95 and 99).

The physical properties of the DEXSIL polymers were considered. DEXSIL 100, with a glass transition temperature (T_g) of 25°C, is not elastomeric.¹⁰⁰ All of the other DEXSIL polymers are elastomeric, with T_g decreasing from 25°C for (all meta) DEXSIL 100 to -42°C for DEXSIL 200; -68°C for DEXSIL 300; -75°C for DEXSIL 400; -88°C for DEXSIL 500, and finally, -125°C for poly(dimethylsiloxane).¹⁰⁰ There is a linear relationship between $1.0/T_g$ and weight-percent of carborane. Para-carboranes have a higher T_g than do the meta-carboranes: for p-DEXSIL 300, T_g is -35°C.¹⁰¹

Although DEXSIL 200 has a crystalline phase, with a crystalline melting temperature of 68°C, this crystallinity was disrupted by incorporating 30-50% para-carborane as a random copolymer. No crystalline melting temperature was found, indicating a totally amorphous polymer. In addition, substituting phenyl moieties for methyl increased T_g . For example, for DEXSIL 200, including 24% diphenylsiloxane, T_g was -32°C, and at 33% diphenyl, T_g was -24°C; however, the polymer was completely amorphous. With 33% methylphenylsiloxane in the polymer, T_g was -37°C and the polymer was also amorphous.⁹⁹

The substitution of trifluoropropyl groups for methyl in DEXSIL 200 also increased T_g , but rendered the polymer amorphous. For example, T_g was -50°C for DEXSIL 200, and -3°C when three of the methyls were replaced by trifluoropropyl; the linear relationship between $1.0/T_g$ versus weight-percent of trifluoropropyl groups also applied.¹⁰²

One of the unique properties of carborane-siloxanes is their outstanding thermal stability. Among the techniques used for studying thermal and thermo-oxidative stability were TGA, DSC, and TBA. TGA studies have shown that the DEXSIL elastomers degrade severely only above 500°C, whereas polydimethylsiloxane was severely degraded at temperatures slightly above 400°C. Replacement of para- for meta- results in reduced weight loss, as does replacement of phenyl for methyl. The fluorinated polymer has a stability that is intermediate between those of polydimethylsiloxane and nonfluorinated DEXSIL. Roller and Gillham believe that the cyclization mechanism of degradation of polydimethylsiloxane is not operative for the polycarboranesiloxanes.¹⁰⁰ The TBA showed that nearly all the m-DEXSIL elastomers stiffened abruptly near 550°C as a result of crosslinking resulting from heating in an inert atmosphere. Hence, in an inert atmosphere, m-DEXSIL 300 is the most stable of this class of polymer, although DEXSIL 200 is also very stable.

The thermo-oxidative behavior of the DEXSIL elastomers was studied by Roller and Gillham.¹⁰³ They observed that pure polydimethylsiloxane experienced virtually all of its weight loss below 400°C, the temperature corresponding to the onset of weight loss in an inert atmosphere. All of the DEXSIL elastomers began stiffening around 300°C, indicating a substantial increase of crosslink density due to oxidation. Of interest is that pure polydimethylsiloxane, which began stiffening around 350°C, was more stable from an oxidative point of view. According to TGA, the fluorinated DEXSIL elastomers were less

stable, with weight loss commencing near 300°C and a high rate of weight loss around 350-375°C. Hence, there is the possibility of making crosslinked polydimethylsiloxanes that are inherently more oxidatively stable than DEXSIL elastomers, so long as the crosslinks are not the weak links.

A few conclusions are that weight retention to 800°C decreases linearly with the number of dimethylsiloxanes in the chain; that addition of carborane blocks impedes siloxane chain depolymerization; that substitution of phenyl for methyl groups results in increased weight retention, probably because of increased crosslinking; and that very high molecular weight polymer actually shows a weight gain to 800°C, probably because oxidative crosslinking more than compensates for degradation. (see Ref. 12, p. 107).

Stress relaxation determinations of a series of DEXSIL 300 elastomers have shown that, in air, oxidative crosslinking begins around 275°C for unfilled DEXSIL 300, although DEXSIL 200 does not show oxidative crosslinking under 340°C.¹⁰⁴ The oxidative reaction for ferric oxide filled DEXSIL 300 begins around 300°C.

Regarding the formulation of DEXSIL materials, Peters indicated that an amorphous silica filler enhances the mechanical properties of the elastomer, but that it results in a rapid deterioration of properties at 315°C, owing to surface silanol groups.⁹⁶ However, hydrophobic silica, pretreated with a trimethylsilylating agent, produces vulcanizates with good mechanical properties after aging at 315°C in air. (Elongation decreased from 100 to 45% after 150 hours, for example.) As with most elastomers, increased elongation is achieved by increasing the molecular weight of the gumstock. Of the oxidative stabilizers, ferric oxide has been shown to be very effective: for example, without it, oxidative crosslinking begins in 2.5 hours at 300°C, but with 10 ph ferric oxide, oxidative crosslinking is delayed to about 9 hours. In phenyl-modified DEXSIL 200, addition of 10 or 15 phr ferric oxide resulted in elastomeric properties after 1000 hours at 315°C, 24 hours at 427°C or 2 hours at 482°C. For DEXSIL 200 (33 mole% methylphenyl-modified), with 30 phr hydrophobic silica, 2.5 phr ferric oxide, and 2.5 phr dicumyl peroxide for vulcanization, the elongation was 100%. Upon heat aging in air at 300°C for 150 hours, elongation was 45%; for 24 hours at 343°C, elongation was 30%, and upon heat aging for 4 hours at 371°C, elongation was 15%. These results suggest a practical long-term upper use limit of DEXSIL 200 vulcanizates of 315°C, and a short-term exposure temperature of 340°C.

Finally, as with the fluorosilicones, increased solvent resistance was obtained when trifluoropropyl groups were substituted for the methyl.⁹⁶ An important point to be made is that much of the science and technology developed for the DEXSIL elastomers has potential value in developing the technology of other types of siloxane block copolymers. Regarding the economics of DEXSIL elastomers, a study indicated that the anticipated cost of the dodecacarborane would be on the order of \$200/lb for production of 100,000 lb/yr and on the order of \$100/lb for production of 1,000,000 lb/yr.¹² One company the author contacted quoted a price of \$25,000/lb for quantities less than 1 pound, with discounts for quantities greater than 1 pound. Until major breakthroughs are made in the economic production of the carborane, the DEXSIL elastomers will remain a very specialized material with fairly limited applications, such as a stationary phase in gas chromatography.

SILPHENYLENE-SILOXANE COPOLYMERS

Analogous to the DEXSIL family of elastomers, there are also a number of siloxane block copolymers in which the block unit is phenylene or one of its derivatives. Not as much effort has been expended in the development of this family of elastomers, but the potential for thermally stable elastomers is considerable. Polysil-p-phenylenes are very resistant to heat because of their inability to undergo cyclization.²⁸ Introduction of the silarylene unit into the siloxane serves to prevent thermal unzipping to cyclic products because of the aromatic character of the silarylene unit. This is seen by comparing the thermal degradation temperature of a typical polydimethylsiloxane, 350°C, to poly(tetramethyl-p-silylphenylene siloxane), at 450°C (Ref. 12, p. 144).

The monomer for the preparation of silarylene siloxanes is generally p-bis(hydroxydimethylsilyl)benzene. The polymers from this monomer can be made by several methods. Self-condensation is catalyzed by alkali metal hydroxides. To make copolymers, the hydroxyl monomer can be co-condensed with dialkyl(aryl)dichlorosilane or bis-chloro terminated siloxanes. Breed et al. described the preparation of the siloxane copolymer by treating the hydroxyl monomer with cyclic N-methylsiloxazenes; they succeeded in making polymers with two, three, and four dimethylsiloxane units in the monomer unit.^{105,106} Dvornik described the condensation of the hydroxyl monomer with bisureidosilane units, and made exactly alternating silarylene-siloxane polymers of fairly high molecular weight, which are similar to the DEXSIL 200 elastomers.¹⁰⁷ Pittman et al. described the preparation of the silarylene-siloxane copolymers by treating the hydroxyl monomer with bis-dimethylamino-terminated silane or siloxane groups to make polymers of molecular weights above 100,000.¹⁰⁸

The physical properties of the silarylene-siloxanes resemble those of the DEXSIL elastomers. The T_g of the silphenylene-siloxanes, as might be expected, decreases as the number of dimethylsiloxy units increases in the monomer unit, from -21°C for the unit containing one siloxy unit¹⁰⁹ to -102°C for four siloxy units in the monomer unit (Ref. 12, p. 155). Likewise, replacing methyl with phenyl increases T_g , and replacing the phenylene block with a larger unit, such as diphenylether, increases T_g . (For three dimethylsiloxy units, T_g for the diphenylether block is -37°C, whereas for the p-phenyl block, T_g is -62°C. Of interest is the observation that substituting meta-phenylene for para-phenylene as the block unit rendered the elastomer amorphous.

The thermal stability of the silphenylene-siloxanes has been evaluated primarily by TGA. It is determined by the nature of the silarylene unit, the number of siloxane units per silarylene unit, and the nature and number of substitution of some other groups for methyls.

Merker and Scott evaluated the thermal stability of poly(tetramethyl-para-silphenylene monosiloxane) by heating in air.¹¹⁰ After 16 hours at 305°C, the silphenylene polymer was slightly yellow in color, but remained pliable with about 6% weight loss, whereas a sample of polydimethylsiloxane treated under the same conditions changed to a hard, brittle gel with 25% weight loss. The thermal decomposition in nitrogen was considered for a series of para-silphenylene copolymers with various numbers of dimethylsiloxanes in the polymer unit; the thermal stability was found to decrease with an increase in the proportion of dimethylsiloxane groups.³ It was found that polydimethylsiloxane was less stable than any of the other polymers examined; a rapid increase in weight loss was observed at 390°C.¹⁰⁸ However, the p-silphenylene-monosiloxane copolymer required 500°C for rapid weight loss. It

was proposed that the main reactions were chain scission between the silicon and phenylene bond and hydrogen evolution arising from the decomposition of methyl substituents. There was no thermal rearrangement to cyclic siloxanes, since the silphenylene group sterically hinders ring formation because of the inability of the helix structure of the polymer to form.

Pittman et al. reported that, although polydimethylsiloxane began its weight loss (nitrogen) around 250°C and lost 20% of weight around 380°C, the temperature for 20% weight loss for some p-silphenylene copolymers is higher.¹⁰⁸ For the mono-dimethylsiloxane copolymer, this temperature was 410°C, and for the mono(diphenylsiloxy) copolymer, the temperature for 20% weight loss was 480°C. Therefore, the thermal stability was found to increase when phenyls were substituted for methyls. Burks et al. have shown that, when the siloxane group was phenylmethyl, the thermal and thermo-oxidative stability was higher than for the dimethylsiloxane group.¹¹¹ The temperature corresponding to 10% weight loss for the first group was 460°C, and for the second group, 440°C. Likewise, the weight loss after heating in air at 316°C for 11 hours showed 7% for the phenylmethyl group and 31% for the dimethyl group.

Breed et al. indicated, on the basis of TGA measurements in nitrogen for silphenylene copolymers containing three dimethylsiloxane groups in the monomer unit, that the thermal stability (and temperature for 20% weight loss) follows the sequence p-diphenylether (600°C) > p-phenylene (560°C) > m-phenylene (510).¹⁰⁵ (These results are similar to those of Dvornik, where the onset of degradation was 410°C for the ether-diol and 400°C for the p-silphenylene unit, where the number of dimethylsiloxanes equaled the silphenylene units.)¹⁰⁷ Also of interest was that stability in nitrogen increased for an increasing number of vinyl groups substituted for methyl. Breed et al. also showed, for p-phenylene ether blocks, that thermal stability decreased with an increasing number of dimethylsiloxy groups in the monomer unit.^{105,106,112} The number of groups, and the temperature corresponding to 20% weight loss, is as follows: two, 600°C; three, 570°C; and four, 520°C. These results correspond to those of Goldfarb et al., who found the same trend with a series of xylylenesiloxane-dimethylsiloxane copolymers, where 25% weight loss ranged from 535-560°C.⁴³ Of interest in that paper is a very high decomposition temperature for polydimethylsiloxane (initial weight loss around 350°C and 25% weight loss around 430°C, in contrast to the results of others,¹⁰⁸ which have corresponding temperatures of 250 and 380°C). The reason for the silicone thermal stability is that Goldfarb's silicone was carefully prepared by the tetramethylammonium hydroxide catalyzed ring-opening polymerization of cyclic siloxane tetramer and, as mentioned earlier in this report, silicones prepared with that catalyst have shown good thermal stability.

There has been substantial effort to produce trifluoropropyl derivatives of these polymers, in addition to work done to introduce perfluorinated moieties capped by phenyls as the silphenylene block. The first group is called FASIL elastomers. These elastomers, designed for solvent resistance at elevated temperatures, were bis(methyltrifluoropropyl)-meta silphenylene copolymers with two methyltrifluoropropylsiloxane units.¹¹³ TGA indicated 50% weight loss at temperatures slightly above 500°C in inert atmosphere and at 455-497°C in air. The lower decomposition temperatures for these materials were also found by Goldfarb.⁴³ For the same polymer the temperature of 25% decomposition was 450°C, and substitution of fluorinated groups was found to decrease the thermal stability.

There is very little information regarding the processing of these elastomers. Burks et al. used in some cases colloidal silica, along with partially hydrolyzed ethyl silicate, with dibutyltin diacetate for *p*-bis(dimethylsilyl)phenylene and either dimethylsiloxane or methylphenylsiloxane copolymer.¹¹¹ They obtained elastomers with elongations of 530-1170%.

It has been stated (Ref. 12, pp. 161-2) that, based upon the possibility of high molecular weight (250,000 to 1,000,000) along with the other properties described, there are substantial possibilities for uses of the silphenylene-siloxane copolymers as high-temperature elastomers. It was concluded that a product cost of around \$30/lb is anticipated in large scale-up. Another factor, however, comes to mind. The silphenylene monomer, bis(hydroxydimethylsilyl)benzene, has invariably been made by Grignard coupling of dibromo (or chloro) benzene with dihalodialkylsilane, followed by hydrolysis.^{107,108,110,112-123} There are also a few papers dealing with alkali-metal coupling to accomplish this.^{124,125}

The industrially important field of organopolysiloxane chemistry was founded upon the Grignard process in the early 1940s. That process was versatile and afforded a ready route to the required organochlorosilane intermediates, but the raw materials were costly and the large amounts of solvent required made for a process of low volume efficiency. Unfortunately, these methods were simply too expensive for production of the required monomer on a large scale. Prior to the discovery of direct synthesis of alkylhalosilanes by the high-temperature reaction of silicon with organohalides (the Rochow process) the silicone industry was very small. Direct synthesis of silicone starting materials was needed to enable the silicone industry to grow. The same is likely true for possible growth of silphenylene-siloxane elastomers. Needed is economic production of the bis(halodiorganosilyl) aromatic block.

In a paper describing the direct synthesis of phenylchlorosilanes, Barry et al. stated that, when 3810 grams of phenyltrichlorosilane, 2440 grams of trichlorosilane, and 64 grams of boron trichloride were heated in a bomb at 290 to 310°C for 16 hours, among the reaction products were 476 grams of *m*-bis(trichlorosilyl)benzene, 141 grams of *p*-bis(trichlorosilyl)benzene, and 356 grams of phenyldichlorosilyl-trichlorosilyl-benzene, and 520 grams of nonboiling, polymeric residue.¹²⁶ They also mentioned that, among the high-boiling products of the reaction of benzene with trichlorosilane, catalyzed by boron trichloride, was found 14.9% hexachlorodisilylbenzene and 9.3% phenylpentachlorodisilylbenzene. In a patent, Clark described a high-temperature reaction leading to the production of organopolysilicon halides in which the silicon atoms were linked by phenylene radicals.¹²⁷ His method was to heat a phenylchlorosilane with aluminum chloride. For example, heating 1774 grams of diphenyldichlorosilane and 8.5 grams of aluminum chloride for 48 hours, at from 210 to 250°C, resulted in 192 grams of bis(phenyldichlorosilyl)benzene and 668 grams of a residue believed to consist of poly(dichlorosilyl)benzene. In another example, he reported a yield of about 10% of bis(phenyldichlorosilyl)benzene by heating diphenyldichlorosilane and 5% aluminum chloride for 2.5 hours. Rust reported that a silane bond would react under heat and pressure with a phenyl group of a phenylsilane to produce bis(silyl)benzene products.¹²⁸ For example, phenyldichlorosilane, when heated to 450-550°C for 8 hours in a closed bomb, gave (phenyldichlorosilyl)-dichlorosilyl benzene; a 1:1 molar mixture of phenyldichlorosilane and methyldichlorosilane, heated in a closed bomb for 7 hours at 400-500°C, gave dichloromethylsilyl-dichlorosilyl benzene.

It appears that there is a possibility of producing the monomer through direct synthesis. Some of the direct synthesis chemistry developed in the early days of silicone technology should be experimentally re-examined, either to make the monomer directly, or to use by-products of existing processes as a source for the monomer, bis(halodiorganosilyl)benzene.

SILOXANE BLOCK COPOLYMERS--MISCELLANEOUS

The final section of this paper deals with various other types of siloxane block copolymers that have been presented in the literature. In general, the science and technology of these copolymers is not as advanced as that of the other elastomers discussed; nevertheless, some of them may offer potential for further development.

The preparation and properties of cyclosiloxane block copolymers with dimethylsiloxane were described by Andrianov.¹³⁴⁻¹³⁵ The method for preparing these copolymers was via the disilane-terminated polydimethylsiloxanes with cyclosiloxanes containing two vinyl groups. In these papers, the cyclosiloxanes were dimethyl or diphenyl; there were either single or multiple rings; and the number of dimethylsiloxanes, compared to the number of rings, ranged from 1 to a large number; e.g., 400. In none of the papers was the polymer described specifically as an elastomer, although it was commented that, as the ratio of dimethylsiloxane groups to cyclic groups increased, the T_g decreased, as well as the thermal stability, which ranged from 350 to 400°C, for initial TGA decomposition. This area of research may be very promising, and deserves further effort.

Spirosiloxane elastomers were described by Andrianov as being prepared by the tetramethylammonium hydroxide catalyzed polymerization of various spiro-siloxanes.¹³⁴⁻¹³⁶ The products were elastomeric, with TGA decomposition temperatures of 380-390°C, and were crosslinked when prepared.

Silicon phthalocyanine block copolymers have been prepared from silicon phthalocyanine dichloride and dimethylsiloxane units.¹³⁷ The monomer, silicon dichlorophthalocyanine, was prepared by the reaction of silicone tetrachloride with 1,3-diiminoisoindoline in tributylamine in solvent.¹³⁸ A semicommercial process based on this has been developed; the monomer was found stable to 450°C. In preparing the polymer, the silicon phthalocyanine dichloride is hydrolyzed to the diol, treated with two equivalents of methylphenyldichlorosilane, hydrolyzed to make the corresponding diol, treated with two equivalents of dichlorodimethylsiloxane, hydrolyzed to the diol, and then treated with the bis(ureido)-tetra(dimethylsiloxane) to make a polymer of molecular weight 12,000 which is soluble in polar organic solvents and stable at 300°C. No mention was made concerning the elasticity of the polymer, but if elastomers could be made by this route or by some other, less expensive method (e.g., by elimination of the ureido step) then such elastomers should easily outperform silicones in heat stability.

Polycycloalkylene-siloxane polymers were prepared by the chloroplatinic acid-catalyzed addition of two moles of chlorodimethylsilane with cyclopentadiene to make the bis(chlorodimethylsilyl) adduct. This, when hydrolyzed, formed a stiff gum (T_g , -11°C), which was thermally stable in nitrogen to 400°C.¹³⁹ This silane-olefin addition approach to making

blocks appears to be potentially as promising as the direct synthesis method of making bis(haloalkylsilyl)benzene blocks for siloxane copolymers.

There are a few examples of siloxane-imide copolymers in the literature.¹⁴⁰⁻¹⁴⁴ These were made by several methods, which generally involved either the diacid or anhydride reaction with diamine. Unfortunately, either the siloxane chain length was so long (about 35 units) that the polymer had insufficient blocks to effect thermal stabilization, or it was so short that the T_g was too high. Since polyimides are quite thermally stable, this area of research may bear further investigation.

There are a number of papers dealing with miscellaneous types of siloxane block copolymers. Examples are those dealing with polyphenylether blocks,^{145,146} s-triazine blocks,¹⁴⁷ polysulfone blocks,¹⁴⁸⁻¹⁵¹ and ferrocene blocks.¹⁵² In every case, either the siloxane blocks were too long (hence providing no thermal stability advantage over silicone elastomers), or the methods of preparation too involved, or the thermal stability was inadequate.

CONCLUSIONS

This review has included the major areas of research and technology in thermally stable elastomers. The research effort in this topic has only been a small part of the research conducted in thermally stable polymers overall; hence, most of the thermally stable polymers are generally fairly hard and, in many cases, intractable materials.

Nevertheless, several areas of research in thermally stable elastomers bear promise for the future. Considerable work still needs to be done in making an "elastomer teflon," since teflon, or polytetrafluoroethylene, is very stable. Du Pont's KALREZ certainly represents a major advance in this field, but the production of a less expensive, and equally stable, material should be worthwhile. Elastomers consisting of perfluoroalkylene or perfluoroalkylene ether units with perfluorotriazine blocks also point to a promising future area of research, although the cost of these materials at present is very high.

Another very promising area for the future is that of the polyorganophosphazenes. Reiterated here is Allcock's statement that this area of technology is presently in the same stage of development as were the silicones in the early 1950s.^{20,31} A number of excellent products based upon polyorganophosphazenes can be expected in the future. Regarding the silicones, much can be done to produce polydimethylsiloxanes which are more thermally stable than those now available. This could be accomplished by simple removal of base catalysts or by preparation using catalysts that are destroyed by heating, such as tetramethylammonium hydroxide. In other words, polydimethylsiloxanes or polymethylphenylsiloxanes have considerable potential of their own. Even so, the most promising area for development of elastomers stable above 400°C lies in the area of block siloxane copolymers. Here, there would be a block of some sort (alkyl or aryl) followed by two to four dimethylsiloxane units. To make these blocks, it is necessary to make a bis(halodiorganosilyl)-block monomer, where the block may be benzene, another aryl group, or an alkyl

(preferably cyclized) group. These monomers can likely be prepared economically either by direct synthesis methods or by use of the silane-olefin addition reaction.

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