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SILICONE MODIFIED RESINS FOR GRAPHITE FIBER LAMINATES

L. W. Frost and G. M. Bower

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December 18, 1980

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Prepared for
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SUMMARY

When graphite fiber composites are burned, the liberated fibers may settle on electrical apparatus and cause severe damage. This problem can be minimized by bonding the fibers with silicone modified laminating resins that leave a siliceous residual char when they are burned.

During the second year of this program, 23 additional silicone modified resins have been synthesized and evaluated for this application. Included were siloxane-silazane-epoxies, siloxane-imide-epoxies, and unsaturated siloxanes. Further evaluation of resins from the first year was also done. Neat resins were judged in terms of Si content, homogeneity, hardness, char formation, and thermal stability. Char formation was estimated by thermogravimetry to 1,000°C in air and in N_2. Thermal stability was evaluated by isothermal weight loss measurements for 200 hrs in air at 200°C.

Six silicone modified resins were selected for evaluation in unidirectional filament wound graphite laminates. Neat samples of these resins had 1,000°C char residues of 6-63%. The highest flexural values measured for the laminates were a strength of 1,220 MPa (177 kpsi) and a modulus of 105 GPa (15.2 Mpsi). The highest interlaminar shear strength was 72 MPa (10.4 kpsi).

INTRODUCTION

This report describes work done in the second and final year of a project to develop silicone modified resins for use in the manufacture of graphite fiber composites. The first year's work has been reported previously.[1] The graphite epoxy composites presently in use are among the strongest and stiffest materials available. They have found use in applications ranging from golf clubs to airplane wings. However, when such composites are involved in a fire that is sufficiently intense to burn off the resin, graphite fibers are released into the air. The fibers are electrical conductors, and if they settle on electrical equipment, severe damage can be done. However, if the matrix resin contains a substantial proportion of silicon it may be expected to leave a nonvolatile solid residue (char) when it burns. This residue is likely to act as a trap for the graphite fibers and minimize their dispersal.

During the first year of the program, 85 silicone modified resins were synthesized and evaluated for this application. Included were unsaturated polyesters, thermosetting methacrylates, epoxies, polyimides,and phenolics. Neat resins were judged in terms of Si content, homogeneity, hardness, char formation, and thermal stability. Char formation was estimated by thermogravimetry to 1,000°C in air and in N_2. Thermal stability was evaluated by isothermal weight loss measurements for 200 hrs in air at three temperatures. Graphite fiber laminates prepared from the most promising candidates were evaluated for flexural strength and modulus and for interlaminar shear strength at room temperature and at 200°C. The best resins were silicone modified epoxies and imide-epoxies, using anhydride cure systems.

The work has now been extended to include the preparation and evaluation of additional silicone modified resin systems. Polymers high in aromatic content and with relatively high crosslink density were prepared in an effort to obtain composites of higher strength and modulus than those previously made. These polymers include siloxane-silazane-epoxies with aromatic amine cure, siloxane-epoxies with aliphatic amine cure, siloxane-imide-epoxies with anhydride cure, a siloxane-phenolic, and a PMR imide-siloxane.

MATERIALS

Organosilicon compounds were obtained from either PCR Research Chemicals, Inc., or Petrarch Systems, Inc. Unless otherwise indicated they were used as-received. Epon 828 was obtained from the Shell Chemical Corp., DER330 from the Dow Chemical Co., and Araldite MY720 from the Ciba-Geigy Corp. Other materials were obtained from the usual laboratory supply companies.

SYMBOLS

A considerable number of complex polymers have been prepared in the course of the project. Nomenclature for such materials becomes very cumbersome unless a system of shorthand symbols is used. The system used in these reports is designed to identify each polymer quickly and concisely and to identify a particular batch of material. A separate system has been devised for each purpose.

Each polymer is assigned an identification number which indicates the general class of material and identifies a particular composition within the class. The following letter designations are used for the various classes:

EpS	epoxy silicone
EpIS	epoxy imide silicone
PS	phenolic silicone
IS	imide silicone
MaS	methacrylate silicone.
VS	vinyl silicone

A number is used with each letter designation. Numbers were assigned consecutively to compositions as they were made for the first time. If a given composition was prepared again it was not assigned a new number unless there was a substantial difference in the method of preparation.

Each batch or specimen is assigned a batch number consisting of three parts: notebook number, page number, and item on the page. Thus, for example, D98-96-2 refers to the second item on page 96 of notebook D98. This number provides a quick reference to the original records and also distinguishes among different batches of the same polymer.

Abbreviations are also used for many of the chemical compounds which are referred to repeatedly. In addition to standard symbols for the elements, the following symbols are used for particular chemical groups or compounds:

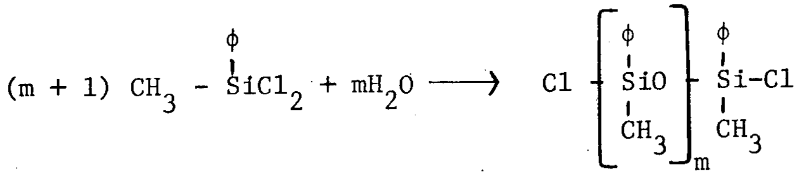
APS	3-aminopropyltriethoxysilane
BPA	2,2-bis(4-hydroxyphenyl)propane
BTDA	3,4,3′,4′-benzophenonetetracarboxylic dianhydride
DDS	4,4′-diaminodiphenylsulfone
DMCS	dimethyldichlorosilane
DMES	dimethyldiethoxysilane
DMF	N,N-dimethylformamide
E8	Epon 828 or DER330 (diglycidyl ether of BPA)
GPS	3-glycidoxypropyltrimethoxysilane
HXA	hexamethylenetetramine
MAPS	3,methacryloxypropyltrimethoxysilane
MDA	4,4′-methylenedianiline
MOE	2-methoxyethanol
MPCS	methylphenyldichlorosilane
MPD	m-phenylenediamine
MPMS	methylphenyldimethoxysilane
MY	Araldite MY720
NBA	5-norbornene-2,3-dicarboxylic anhydride
PCS	phenyltrichlorosilane
PMDA	pyromellitic dianhydride
PMS	phenyltrimethoxysilane
TBP	tert-butyl perbenzoate
TEA	triethylamine

THF	tetrahydrofuran
VCS	vinyltrichlorosilane
VES	vinyltriethoxysilane

RESULTS AND DISCUSSION

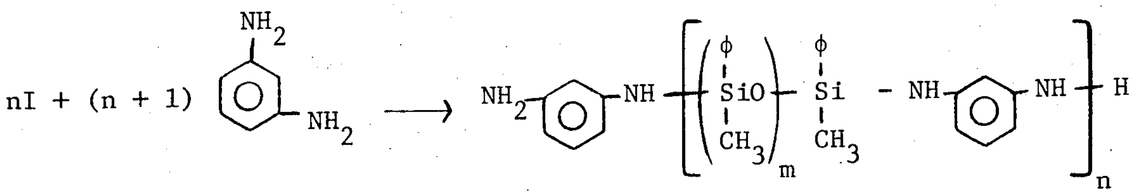
Polymer Preparation and Chemistry

Siloxane-Silazane-Epoxies. - Chloro terminated siloxane oligomers, prepared by partial hydrolysis of chlorosilanes, react readily with aromatic amines to give products containing both siloxane and silazane linkages. In the present work, triethylamine (TEA) was used as an acceptor for the HCl produced as a by-product. When the aromatic amine is difunctional and is used in excess, amine terminated siloxane-silazanes are produced, which can be used as epoxy curing agents. For example, methylphenyldichlorosilane (MPCS) and m-phenylenediamine (MPD) give reactions and products as follows:



$$(m + 1)\ CH_3 - \overset{\phi}{Si}Cl_2 + mH_2O \longrightarrow Cl - \left[\underset{CH_3}{\overset{\phi}{Si}}O\right]_m - \underset{CH_3}{\overset{\phi}{Si}}-Cl \qquad (1)$$

I



(2)

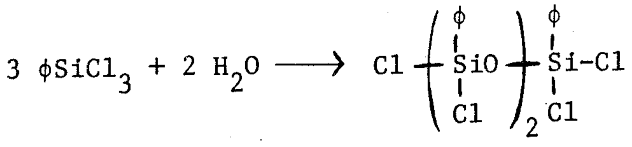
II

Both I and II consist of mixtures of molecules of various chain lengths in which m and n $\geqq 0$. The most satisfactory properties were found in polymers derived from intermediates in which the average value of m was 2-3 and n was 0.8-1.0.

The hydrolysis reaction was carried out by slowly adding a solution of water in tetrahydrofuran (THF) to a rapidly stirred solution of the chlorosilane in THF. This method maintains a one phase reaction medium and minimizes locally high water concentrations. These precautions have been found to produce a product mixture having a relatively narrow range of molecular weights.[2,3]

The average value of m in product I is determined by the ratio of reactants. However it is rather difficult to eliminate adventitious water in handling the solutions and filtering off the solid by-product. Consequently the actual value of m is usually somewhat higher than the value calculated from the amount of water added deliberately. Oligomers of the desired average chain length were conveniently prepared by blending appropriate quantities of two batches, one of which was a little higher, the other a little lower than the desired value. The values of m were determined by complete hydrolysis of the chlorosiloxane and titration of the liberated HCl with standard NaOH.

Branched chain and crosslinked molecules can also be produced by reaction of the secondary amine H atoms of II with additional chlorosiloxane. Apparently this reaction is not very significant under the conditions employed, since oligomers prepared from dichlorosilanes and diamines showed no tendency to gel at the reactant ratios used. Crosslinking and gelation became significant factors, however, when the functionality of the chlorosilane was greater than 2. In one series of preparations, phenyltrichlorosilane (PCS) was used as the source of siloxane groups. Although this monomer is trifunctional it was found possible to prepare a stable liquid oligomer mixture of the following average composition:

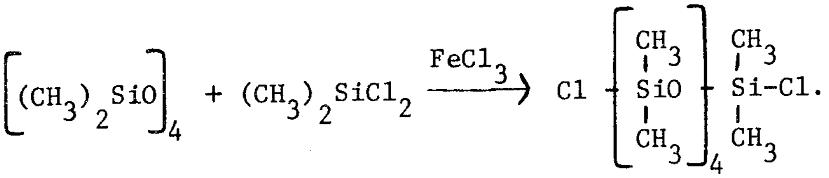


$$3\ \phi SiCl_3 + 2\ H_2O \longrightarrow Cl\left(\begin{array}{c}\phi\\ |\\ SiO\\ |\\ Cl\end{array}\right)_2 \begin{array}{c}\phi\\ |\\ Si\text{-}Cl\\ |\\ Cl\end{array} \qquad (3)$$

III

A similar intermediate was prepared in the same way from three moles of vinyltrichlorosilane (VCS) and two moles of H_2O.

A chloro terminated dimethylsiloxane oligomer was prepared by the following reaction[4]:



$$\left[(CH_3)_2SiO\right]_4 + (CH_3)_2SiCl_2 \xrightarrow{FeCl_3} Cl\left[\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right]_4 \begin{array}{c}CH_3\\ |\\ Si\text{-}Cl.\\ |\\ CH_3\end{array} \qquad (4)$$

IV

Reaction of IV with diamines gave another series of amine terminated siloxane-silazanes.

The aromatic amine terminated siloxane-silazane oligomers were found to be effective curing agents for epoxy resins. Two types of epoxies were used. The first was a liquid resin having an epoxy equivalent weight of 185-190, consisting primarily of the diglycidyl ether of bisphenol A. Two commercial materials, Shell Epon 828 and Dow DER330, were used interchangeably under the abbreviation E8. The second type was Ciba-Geigy

Araldite MY720 (abbreviated MY), which is largely composed of the tetraglycidyl derivative of 4,4′-methylenedianiline (MDA). This material has an epoxy equivalent weight of about 122.

Table I lists the siloxane-silazane-amine cured epoxy polymers that were prepared. The polymers derived from a dimethylsiloxane intermediate were generally soft and often heterogeneous. Methylphenylsiloxane intermediates with average chain lengths of 2-4 Si atoms gave homogeneous polymers when other parameters were properly chosen. Longer chain lengths, although desirable because of the resulting higher Si content, gave relatively soft polymers which tended to be heterogeneous. When the chain length was reduced to 1, giving a polysilazane intermediate without siloxane linkages, the resulting polymer was soft and unsatisfactory. Use of the trifunctional silane PCS gave polymers in which crosslinking can occur through siloxane bonds as well as through the epoxy cure. This system gave gelation of the siloxane-silazane intermediate if the NH_2/Cl ratio was too low or if the degree of hydrolysis was too high. However, when properly formulated, polymers of this type had adequate shelf life, and, as will be seen later, gave laminates of high strength.

Many of the cured polymers were heterogeneous. The chief source of this problem probably lies in the random nature of reactions such as (1) and (2). If, as seems likely, the NH_2 and Cl groups on the ends of a growing polymer molecule have about the same reactivity as those in the monomers, I and II will be mixtures including some unreacted diamine. Polymers resulting from the reaction of this residual monomeric diamine with the epoxy compound are probably not compatible with the polymer

TABLE I - SILOXANE-SILAZANE EPOXY POLYMERS

ID No.	Siloxane(1)		Amine(2)	NH_2/Cl	Epoxy(3)	NH/Epoxy		Cured Cake(4)	
	Type	Si Atoms/ Chain				from -NH_2	from -NH-Si	Hardness, Shore D	Appearance
EpS-16	DMS	5	MPD	2	E8	1	0.5	82	Black, opaque
EpS-17	MPS	4	MPD	2	E8	1	0.5	70	Tan, opaque
EpS-18(5)	MPS	1	MPD	1.33	E8	1	1.5	31	Black
EpS-19	MPS	4	MPD	2	E8	0.5	0.25	80	Clear amber
EpS-20	MPS	3	MPD	2	E8	0.5	0.25	82	Clear amber
EpS-21	MPS	2	MPD	2	E8	0.5	0.25	83	Clear brown
EpS-22	MPS	4	MPD	2	E8	0.67	0.33	83	Brown, turbid
EpS-23	PS	3	MDA	2	E8	0.67	0.33	82	Brown, turbid
EpS-24	PS	3	MDA	2	MY	0.67	0.33	82	Brown, turbid
EpS-25	DMS	5	DDS	2	MY	0.67	0.33	--	Cloudy, leathery
EpS-26	DMS	5	DDS	2	E8	0.67	0.33	--	Opaque, leathery + oil
EpS-27	PS	3	DDS	2	MY	0.67	0.33	85	Opaque, heterogeneous
EpS-28	PS	3	DDS	2	E8	0.67	0.33	85	Brown, nearly clear
EpS-29	PS	3	DDS	1	E8	0	1	--	Opaque, brittle
EpS-30	PS	3	MDA	1.6	E8	0.545	0.455	85	Cloudy yellow
EpS-31	PS	3	MDA	1.6	MY	0.545	0.455	85	Cloudy yellow
EpS-34	VS	3	MDA	2	E8	0.67	0.33	84	Dark brown, cloudy

---

(1) DMS = dimethylsiloxane, MPS = methylphenylsiloxane, PS = phenylsiloxane, VS = vinylsiloxane.

(2) MPD = m-phenylenediamine, MDA = 4,4´-methylenedianiline, DDS = 4,4´-diaminodiphenyl sulfone.

(3) E8 = Epon 828 or DER330, MY = Araldite MY720.

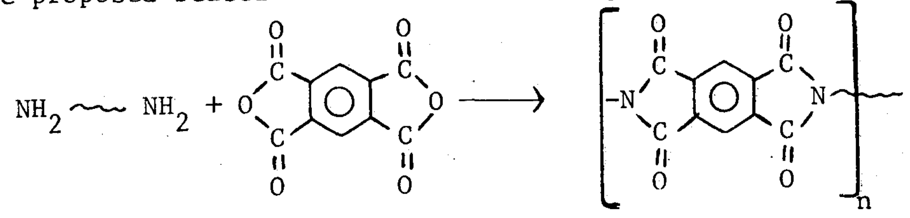
(4) Cure conditions varied somewhat; typically 16 hrs at 150°C.

(5) EpS-18 contained no siloxane linkages. It was prepared from the polysilazane obtained by reaction of MPCS and MPD.

derived from the amine terminated siloxanes. A reduction of the NH_2/Cl ratio in (2) will decrease the amount of unreacted diamine in II, and may be expected to reduce the tendency toward heterogeneity of the final resin. However, when the NH_2/Cl ratio is reduced, premature gelation becomes more of a problem, because the NH groups in the silazane chain are somewhat reactive toward Si-Cl groups and can provide crosslink sites. The problem is more severe when the siloxane is multifunctional, as in III. Polymers EpS-27 through EpS-31 were prepared as an exploration of the limiting NH_2/Cl ratio in this system, using two different diamines. With 4,4´-methylenedianiline (MDA), soluble products were obtained at NH_2/Cl ratios of 2.0 and 1.6, but complete gelation occurred at a ratio of 1.0 (not included in Table I). The less reactive diamine 4,4´-diaminodiphenylsulfone (DDS) gave no gelation at ratios of 2.0 and 1.6, and only a trace of gel at a ratio of 1.0. In this series a ratio of 1.6 gave resins of better clarity and physical properties than were obtained at ratios of 2.0 or 1.0.

Polymer EpS-34 employed three possible crosslinking mechanisms. In addition to siloxane and amine cured epoxy crosslinks, vinyl polymerization could supply additional crosslinks. It was found that cakes of neat resin cured for 2 hrs at 150°C and 3 hrs at 200°C were identical in appearance and hardness whether or not tert-butyl perbenzoate (TBP) was present to act as a vinyl polymerization initiator. However, as shown in a later section, a difference was found in graphite fabric laminates made with and without TBP.

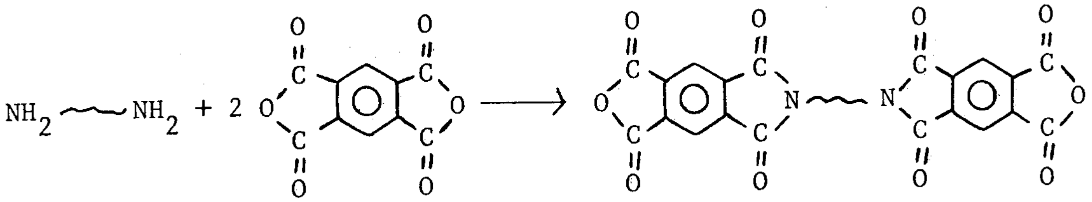
Reaction of PMDA with a siloxane-silazane-diamine: Amino terminated siloxane-silazanes such as II were also considered as intermediates for the preparation of high MW polyimides and of imide anhydride oligomers, which would be useful as curing agents for epoxies. The proposed reactions were the following:



(5)

II

V



(6)

II

VI

However, it turned out that the reactions were not that simple. Attempts to prepare VI and to use it as an epoxy curing agent gave heterogeneous materials with little strength.

An attempt was then made to prepare V by the reaction of pyromellitic dianhydride (PMDA) with the siloxane-silazane intermediate for EpS-17, using the incremental addition method of Bower and Frost.[5,6] A solution of the diamine was stirred while PMDA was added in increments. Viscosity measurements of the solution were made periodically to monitor the course of the reaction. Typically, the viscosity rose after each addition. Early in the run the viscosity increased only slightly after each addition, and then stabilized rapidly. Toward the end, small additions of PMDA gave large viscosity increases, and the viscosity continued to increase for many hours after the addition. Under these conditions it was not practical to wait until the viscosity reached its maximum value after each addition, but the next increment was added when the rate of increase had declined to a low level. The results are summarized in Table II. It is apparent that the equivalence point came at a PMDA/NH_2 ratio of approximately 1.1, rather than the expected 0.5.

To eliminate the problems resulting from the interdependence of reaction time, reactant ratio, and viscosity, the reaction was repeated with a different procedure. A series of mixtures was made, using the same diamine solution, with various amounts of PMDA. The viscosities of the solutions were observed periodically until they became constant. Table III and Figure 1 show the amounts used and the results observed. Maximum viscosity occurred at a PMDA/NH_2 ratio of about 1.02, in approximate agreement with the results of the previous experiment.

A heptane extract of the polymer obtained by baking out the batch with a ratio of 1.03 was a colorless oil having an IR spectrum corresponding to methylphenylpolysiloxane. The residue from the extraction was a yellow powder having an IR spectrum corresponding to an aromatic polyimide.

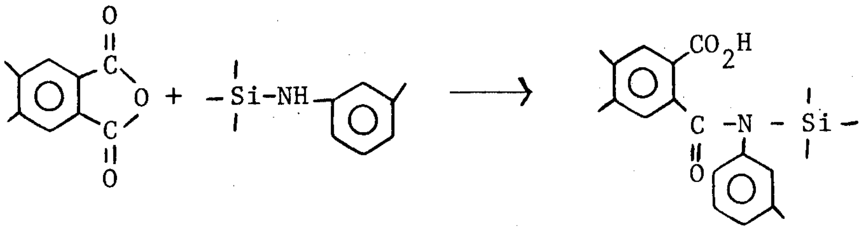
TABLE II - INCREMENTAL ADDITION OF PMDA TO Mps_4-Mpd_2

Total PMDA, g	Ratio, $PMDA/NH_2$	Time From First Addition, Min.	Flow Time, Sec.
0	0	0	<0.1
3.82	0.700	22	0.7
4.55	.834	54	2.1
4.88	.895	83	6.6
4.99	.915	148	10.5
5.12	.939	325	22.7
5.24	.961	441	37.1
5.31	.974	444	41.2
5.31		452	43.4
5.31		1,440	55.3
5.36	.983	1,452	58.2
5.36		1,513	63.7
5.36		1,543	64.2
5.36		1,582	64.8
5.41	.992	1,589	69.2
5.41		1,593	71.6
5.41		1,607	73.5
5.41		1,626	76.0
5.41		1,668	78.2
5.41		1,698	78.3
5.59	1.03	1,711	126.0
5.59		1,722	133.8
5.59		1,766	148.9
5.59		1,828	164.0
5.96	1.09	1,841	192.7
5.96		1,856	205.6
5.96		1,881	216.0
5.96		1,900	224.5
5.96		2,860	134.8
6.08	1.11	2,875	139.6
6.08		2,944	138.4
6.08		2,988	136.1

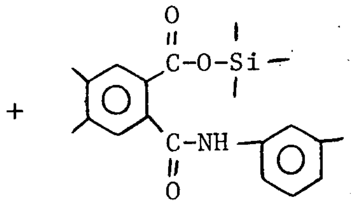
TABLE III - RAPID ADDITION OF PMDA TO Mps_4-Mpd_2

DMAC, g	PMDA, g	Ratio, $PMDA/NH_2$	Viscosity, Stks.
6.22	1.04	0.95	0.85
6.31	1.08	0.99	2.4
6.41	1.12	1.03	3.2
6.50	1.16	1.06	2.0
6.59	1.20	1.10	1.25
6.69	1.24	1.14	0.85
6.78	1.28	1.17	0.65

It is evident that the reaction of PMDA with the siloxane-silazane-diamine caused cleavage of the Si-N bond to give a siloxane and an imide. In addition to the normal reaction of PMDA with the NH_2 groups, reactions of the following types apparently occurred:

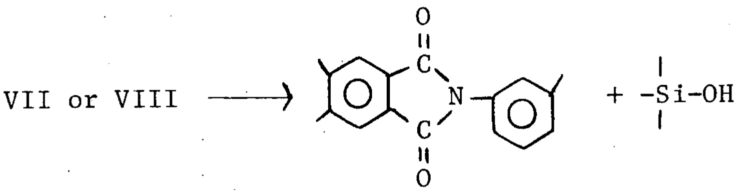


VII



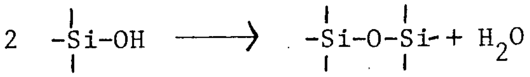
VIII

(7)



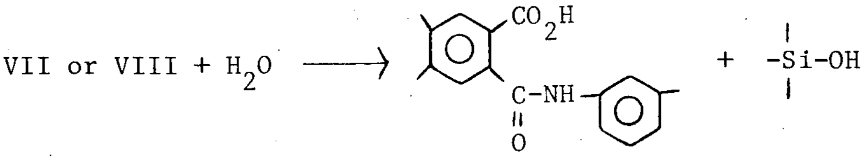
IX

(8)



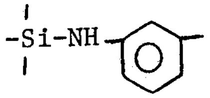
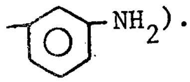
$$2\ -\overset{|}{\underset{|}{Si}}-OH \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O$$

(9)

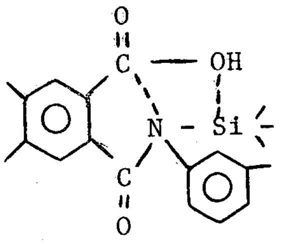


X

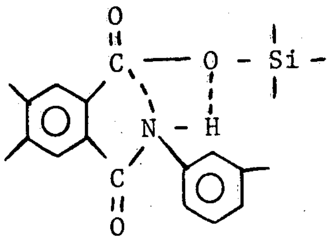
(10)

The formation of structure VIII is suggested by the work of Larsson[7], who obtained $(CH_3)_3Si\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3$ by the reaction of $(CH_3CO)_2O$ with $(CH_3)_3Si\text{-}NH\text{-}CH_2\text{-}C_6H_5$. Both VII and VIII would be crosslinked structures. Since there was no indication of gelation in the experiments that were run, it appears that conversion of VII and VIII to IX and X is more rapid than the initial reactions. The final products would be a linear polysiloxane and a linear polymer containing structures IX and X. For each equivalent of structure IX in the polymer molecule we expect to have three equivalents of structure X (one from  and two from ).

The instability of structures VII and VIII probably results from the ease of formation of cyclic intermediates such as



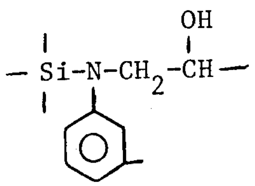
and



,

in which a shift of electrons leads to the formation of the energetically favored imide and $-\overset{|}{\underset{|}{Si}}\text{-}OH$ linkages.

When amine terminated siloxane-silazane intermediates are used directly as epoxy curing agents, structures of the type



are probably not formed in addition to the normal reaction products of NH_2. Elimination of -Si-OH from such a structure does not occur readily because there is no convenient way for the residue to stabilize itself.

Siloxane-Epoxies From Aminopropylsiloxanes. - Amine cured epoxy silicones from aminopropylsiloxanes were studied briefly under Contract NAS3-21373. The aliphatic amino group in these systems is a more active epoxy curing agent than the aromatic amino group present in the amine terminated siloxane-silazanes of the preceding section. Consequently, the polymers were found to cure too rapidly for convenience in making laminates from a B-stage prepreg. However, the partially cured polymers can be prepared as highly concentrated solutions which produce a minimum of volatile by-products on further cure. The volatiles that are produced consist in part of solvent and in part of the alcohols and water produced in siloxane formation. Reduction of these by-products to a low level facilitates the fabrication of laminates of low void content.

Table IV lists four polymers of this type which were made to see if the volatiles could be reduced even further by a more complete condensation to siloxane while the system was still fluid, before the epoxy cure occurred. Since the R/Si ratio in the systems used was less than 2, there was a possibility of gelation from siloxane functionality alone during this condensation.

Conventional epoxies: A polysiloxane was prepared by cohydrolysis of 1 mole of 3-aminopropyltriethoxysilane (APS) and 2 moles of methylphenyldimethoxysilane (MPS) with 3.5 moles of H_2O. The product was evaporated in a N_2 stream to give a colorless, moderately viscous liquid

TABLE IV - SILOXANE-EPOXIES FROM AMINOPROPYLSILOXANES
(AMINE CURE)

	Aminopropylsiloxane Composition, Moles			Cured Cake			
						Wt., g	
ID No.	APS(1)	MPMS(2)	Epoxy	Hardness, Shore D	Appearance	Calc.	Found
EpS-8	1	2	E8	81	Clear yellow, few small bubbles	36.52	37.93
EpS-9	1	2	(3)	45	Clear yellow, badly cracked	35.31	33.84
EpS-32	1	2	MY	81	Clear yellow, flawless	18.12	18.62
EpS-33	1	3	MY	84	Clear amber, flawless	28.30	28.70

---

(1) 3-Aminopropyltriethoxysilane

(2) Methylphenyldimethoxysilane

(3) A polysiloxane prepared by cohydrolysis of 1 mole of 3-glycidoxypropyltrimethoxysilane and 2 moles of methylphenyldimethoxysilane.

having a weight only 8% higher than that calculated for the fully condensed, solvent-free polymer. This product was blended with E8 at a ratio of two epoxy groups per NH_2 group to give a clear liquid, which was cured under vacuum at a gradually increasing temperature (35-100°C) to give a clear cake of polymer EpS-8 about 1 cm thick. This sample weighed 3.9% more than the calculated weight for the completely condensed, solvent-free polymer.

MY was not as soluble as E8 in the siloxanes, and a little THF was added to the uncured mixtures of EpS-32 and EpS-33 to get homogeneous solutions. As before, a ratio of two epoxy groups per NH_2 was used. Slow cure under vacuum at gradually increasing temperatures to a maximum of 120°C gave clear cakes. The final weight of EpS-32 was 2.8%, and that of EpS-33 1.4%, higher than the weight calculated for fully condensed, solvent-free resin.

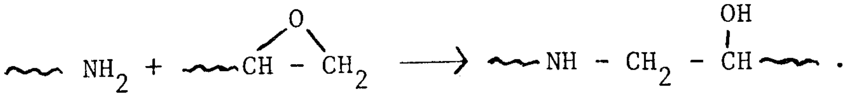
Glycidoxypropylsiloxane: In the case of EpS-9, both the amine group and the epoxy group were present in polysiloxanes. Hydrolysis of the APS-MPMS mixture occurred very readily simply by stirring a mixture of the two monomers with the stoichiometric quantity of H_2O at room temperature. The mixture of MPMS and 3-glycidoxypropyltrimethoxysilane (GPS) hydrolyzed much more slowly, even when a trace of HCl was added as catalyst. One problem with this system is that catalysts for the hydrolysis of the silanes also react with the epoxy group or facilitate its hydrolysis or polymerization. In the present preparation HCl was used as a catalyst and the product was evaporated to 107% of the calculated weight for complete condensation and by-product removal. However, the product was of low viscosity, and the odor of MPMS was still noticeable.

Apparently the hydrolysis of the silanes was incomplete and the epoxy group was partly hydrolyzed. The product was blended with the APS-MPMS hydrolysis product to give a colorless liquid which was cured in the same way as the EpS-8 sample. The resulting cake was soft and badly cracked. Its weight was 96% of the calculated value.

To provide further information on hydrolysis and cure of the glycidoxy silane and siloxane, a sample of the uncured EpS-9 liquid was spread between two salt plates immediately after mixing the two solutions. An IR spectrum was run and then the coated plate was put in the curing oven along with the resin cake sample. Spectra were determined periodically during the heating period. Spectra of both of the individual siloxanes and of the monomers were also run. In addition to the expected features, the spectra of EpS-9 and of the GPS-MPMS siloxane showed a strong OH band at 3,450 cm^{-1}, believed to be due to hydrolysis of the epoxy group. This band was present very weakly in GPS monomer and was absent in APS monomer. The baseline absorbance[8] of the OH band was followed as the cure progressed. Results were as follows:

Cure Schedule, Hrs/°C	Baseline OH Absorbance
0	0.185
24/35 + 4/50	0.304
+20/50	0.272
+24/75	0.195
+24/100	0.148

The increase in OH early in the bake can be attributed to the normal cure reaction:



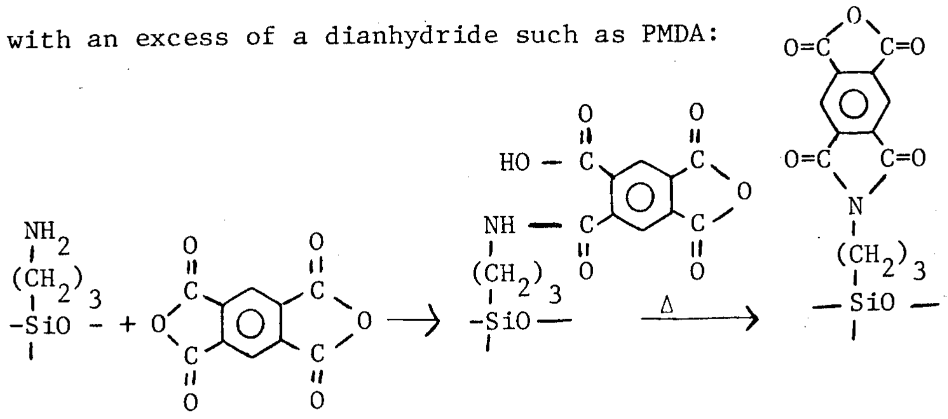
$$\sim NH_2 + \sim \overset{O}{CH - CH_2} \longrightarrow \sim NH - CH_2 - \overset{OH}{CH} \sim .$$

The subsequent decline is less easily explained. Dehydration to an olefin, a polyether, or a morpholine derivative are possibilities, but seem unlikely under the mild conditions employed.

Previous experience with EpS-8 and EpS-9[1] indicated a shelf life of only about 1 hr for these materials. However, samples of uncured EpS-32 and EpS-33 were still liquid after 17 hrs at room temperature. Since their cure rate at room temperature is fairly slow, these materials may give satisfactory B-stage materials. However, the subject was not pursued further because it was expected that polymers higher in aromatic content would give composites with better properties.

Siloxane-Imide-Epoxies. - Polymers in which an epoxy intermediate was cured with a siloxane that incorporated both imide and anhydride groups were studied in the first year. They had satisfactory processing characteristics and char yields, and gave composites with fairly good properties, but strength and modulus were low compared with conventional epoxies. Additional polymers of this type have now been made with higher crosslink density in an effort to improve the physical properties.

The preparative approach included the preparation of a polysiloxane containing 3-aminopropyl groups followed by a two-step reaction with an excess of a dianhydride such as PMDA:

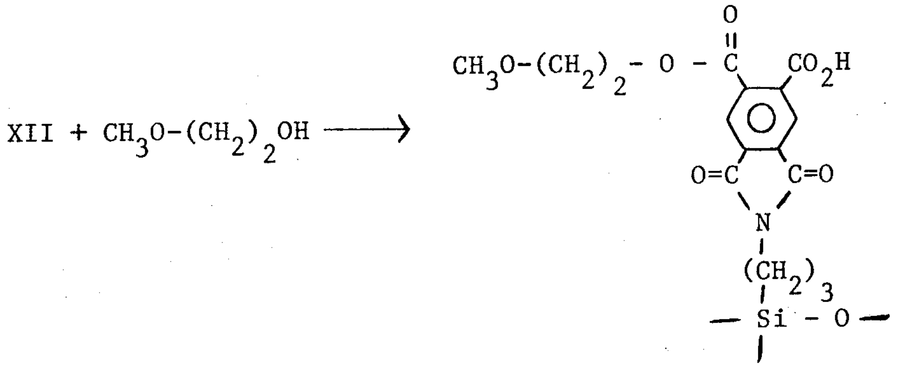


(11)

XI

XII

The polyanhydride XII was then used as an epoxy curing agent. In most preparations XII was reacted further with an alcohol such as 2-methoxyethanol (MOE) to convert some of the anhydride groups to carboxy ester groups before blending with the epoxy:



(12)

XIII

This modification increased the compatibility of the siloxane with the epoxy and also increased the solubility of the combination in conventional solvents such as MOE itself. XIII is still effective as an epoxy curing agent, although less reactive than XII.

The aminopropyl group in these polymers was derived from APS, which is trifunctional with regard to siloxane formation. In order to reduce the functionality and prevent premature gelation, most of the polymers previously prepared were made with the siloxane copolymer used in EpS-8, in which two methylphenylsiloxane units were present for each aminopropylsilsesquioxane unit. Polymers have now been made in which additional siloxane crosslinking was provided by reducing the MPS/APS ratio and also by including phenylsilsesquioxane units derived from phenyltrimethoxysilane (PMS).

Several runs were made in which the stoichiometric quantity of water was added to APS, either neat or in THF solution. Without solvent, a heavy precipitate (insoluble in THF) formed within a few minutes. In THF solution, the time to precipitation increased with THF content, and reached about an hour at a THF/APS ratio of 4-5. Further work was then done at about that concentration. When the solution was reacted with PMDA (1 mole per NH_2), a clear solution in THF was obtained, which was boiled down in a stream of N_2 to 46% solids. An IR spectrum showed the presence of anhydride, imide, and amide groups. When the film on a salt plate was baked at 100°C and 175°C the amide band was eliminated and both imide and anhydride increased (Eq. 11).

A sample of the solution was aged at room temperature with periodic viscosity measurements. The viscosity rose only moderately in about a month (Fig. 2, Curve D98-117-1). Apparently imide formation proceeds well in this system and a rather stable solution is obtained. The solution was cloudy, however, and deposited a small amount of sediment as it aged. The sediment is probably PMDA. Reaction of a mole of PMDA and a mole of $R\text{-}NH_2$ would be expected to give some diimide as well as the desired imide-anhydride. Consequently, some PMDA would be left unreacted. This is not a serious problem, since the PMDA will react with the epoxy component and be incorporated into the final polymer. Reaction with PMDA apparently stabilized the solution of hydrolyzed APS. The aliphatic NH_2 group in APS is an effective catalyst for hydrolysis of alkoxysilanes, and probably also for condensation of silanol groups with each other and with alkoxysilane groups. Conversion of the NH_2 to amide and imide groups presumably reduced its catalytic activity.

A freshly prepared solution similar to D98-117-1 was blended with E8 at an anhydride/epoxy ratio of 0.85 to give polymer EpIS-3. At 68% solids it was a viscous, clear amber solution which was a very viscous fluid after 24 hrs at room temperature. Samples were baked at temperatures up to 200°C to give hard foams. IR spectra of a sample of the polymer that was baked at progressively higher temperatures showed rapid elimination of amide and a progressive decrease of anhydride and epoxy, although both groups remained moderately strong after 2 hrs at 225°C. Imide remained strong. For comparison a paste of PMDA and E8 was baked out, with periodic observation of IR spectra. Even after 5 hrs at 275°C, both anhydride and epoxy bands were present, although greatly diminished. Apparently complete reaction of this system is very difficult to achieve, presumably because of steric hindrance and reduced mobility as the reaction proceeds.

A series of polymers was also made from various combinations of APS, MPS, PMS, PMDA, and E8, using MOE to make a half ester of the anhydride. By varying the ratio of reactants, the R/Si ratio, the total crosslink density, and the Si content of the polymers were varied. In these preparations excess MOE was added to the solution after the PMDA had been reacted in. After adding the E8, the solutions were concentrated to 50% solids. At this point most of the THF had been evaporated, and the solvent was primarily MOE. The compositions are summarized in Table V.

Samples of the polymer solutions were stored at room temperature, and periodic viscosity measurements were made. Results are shown in Figs. 2 and 3. As expected, the resins with the highest epoxy content increased in viscosity most rapidly and gelled most quickly. The shelf

TABLE V - SILOXANE-IMIDE-EPOXIES

ID No.[1]	Batch No.	APS		PMS		MPS		PMDA		E8		R/Si
		g	Moles	g	Moles	g	Moles	g	Moles	g	Moles	
EpIS-3E	D98-113-3	4.17	.0189	--	--	--	--	4.11	.0189	4.11	.0111	1.0
	D98-113-4	3.35	.0151	2.99	.0151	--	--	3.29	.0151	3.30	.0089	1.0
	D98-113-5	2.80	.0127	5.02	.0253	--	--	2.76	.0127	2.76	.0075	1.0
	D98-113-6	2.41	.0109	6.47	.0326	--	--	2.37	.0109	2.38	.0064	1.0
	D98-114-1	3.33	.0151	1.80	.009	1.10	.006	3.29	.0151	3.29	.0089	1.2
	D98-114-2	2.79	.0126	3.49	.0176	1.38	.0076	2.75	.0126	2.75	.074	1.2
	D98-114-3	2.45	.0111	4.82	.0243	1.61	.0088	2.41	.0111	2.41	.065	1.2
EpIS-4	F68-15-1	44.27	0.2	--	--	18.23	0.1	43.63	0.2	43.65	0.118	1.33
EpIS-5	G60-35-1	22.14	0.1	--	--	36.34	0.2	21.81	0.1	14.35	0.0295[2]	1.67

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(1) A terminal letter E indicates that the anhydride group was esterified with MOE.

(2) The epoxy in this case was MY rather than E8.

life is adequate in all cases, since the last step in the preparation can be a simple blending of two stable liquids. A fresh batch could be mixed each day without difficulty.

Samples of the polymer solutions were baked out at temperatures up to 250°C to give clear, bubbled resins. The final weights were about 10% higher than the calculated values. It seems likely that some MOE was retained, either as PMDA ester or as an addition product with the epoxy.

Two other polymers of this general type were prepared. EpIS-4, and the corresponding MOE ester version EpIS-4E, employed an APS/MPS ratio of 2; EpIS-5 used a ratio of 0.5, with MY instead of E8 as the epoxy component. An anhydride/epoxy ratio of 0.85 was used in both types.

Siloxane-Phenolic. - In the first year's work[1] a series of silicone modified phenolic resins was made by reaction of chloro terminated siloxane oligomers, such as I, with an excess of 2,2-bis(4-hydroxyphenyl)-propane (BPA). The resulting intermediates were cured with hexamethylenetetramine (HXA). The polymers were not fully evaluated at that time. One of the most promising compositions, PS-2, has been prepared on a larger scale for evaluation in a graphite composite. A siloxane similar to I ($m = 3$) was reacted with BPA at a BPA/Cl ratio of 1, using a procedure similar to that of Kambour, et al.[4] A solution of HXA in MOE was added (HXA/BPA = 0.285), and the resulting solution was used for composite fabrication.

Siloxane-Imide. - Another class of polymers that was examined briefly in the first phase of the work[1] was silicone modified PMR polyimides.[9] One of the best compositions of this type (IS-1) was selected for evaluation in a composite. This polymer was synthesized from a polysiloxane prepared by cohydrolysis of 2 moles of MPMS and 1 mole of APS. The side-chain NH_2 groups were reacted with a mixture of the methyl half esters of 3,4,3′,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 5-norbornene-2,3-dicarboxylic anhydride (NBA). The BTDA/NBA/NH_2 ratios were 1/2/4. A sample baked out at 225°C was clear amber with a Shore D hardness of 80.

Siloxanes with Vinyl Crosslinking. - As part of the first phase of this project[1], polysiloxanes were prepared in which crosslinking was achieved by polymerization of an unsaturated substituent. The substituents employed were vinyl, derived from vinyltrichlorosilane (VCS), and 3-methacryloxypropyl, derived from 3-methacryloxypropyltrimethoxysilane (MAPS). Additional work with these materials has been done during the second year.

Mention was made in a previous section of a polymer (EpS-34) in which both vinyl and epoxy crosslinking were employed. Polymers were also evaluated in which vinyltriethoxysilane (VES) and MAPS provided the only non-siloxane polymerization. Table VI gives the compositions of the polymers in this group. All except VS-1 were repeat preparations (with modifications) of polymers previously reported[1]. The monomer mixtures were hydrolyzed with a slight excess of H_2O containing a trace of HCl. Most of the volatile by-products were evaporated in a stream of N_2, and the resulting liquid polymers were mixed with 1% of TBP and cured at 125°C. The cured cakes were clear yellow, with many cracks. Hardnesses are given in Table VI. VS-1 and MaS-5 differ only in the nature of the crosslinking

TABLE VI - UNSATURATED SILOXANES

ID No.	Reactants, Moles MAPS	 VES	 MPMS	 DMES	Cake Hardness, Shore D	Viscosity at 25°C, Gardner Initial	 24 Hrs	 48 Hrs	 72 Hrs
MaS-1	1	--	--	--	92	--	--	--	--
MaS-3	2	--	1	--	90	--	--	--	--
MaS-5	1	--	2	--	81	U-V	X-Y	Z1-Z2	Z2-Z3
MaS-10	1	--	--	2	82	C	D-E	--	D-E
VS-1	--	1	2	--	soft	--	--	--	--

group. It appears from the results that the methacrylate group is a much more effective crosslinker than the vinyl group in this system.

Shelf life data for two of the polymer-initiator mixtures are included in Table VI. The stability is adequate for most purposes, since the initiator and polymer are both liquids, and can easily be blended shortly before use.

The silicone-methacrylate polymers described above were made by preparing a methacrylate modified polysiloxane first and then crosslinking by peroxide initiated polymerization of the methacrylate. This method tends to produce a polymer having long siloxane chains and relatively short polymethacrylate crosslinks. Another approach is to polymerize through the methacrylate group first and then crosslink with siloxane linkages. Polymers made in this way may be expected to have a higher modulus and Tg than the first type because the long main chains of the molecules will be relatively rigid polymethacrylates, and the more flexible siloxane linkages will be present only as short crosslinks. The final cure in the first case is a vinyl polymerization, which has the advantage that no volatile by-products are produced and the disadvantage that a suitable B-stage resin is difficult to obtain. In the second system, water and alcohols are produced in the final cure, but this is probably not a serious problem for laminate preparation, since solvent will normally be coming off at that time anyway. Stepwise condensation reactions, such as those leading to siloxanes, tend to produce fusible low polymers, susceptible to further cure, whereas free radical initiated vinyl polymerization tends to go completely or not at all. Therefore, the siloxane cure of the second approach may be expected to give a better B-stage resin.

To test the feasibility of this approach, the monomer mixtures for MaS-1, MaS-3, and MaS-5 were mixed with TBP and polymerized at 155°C in the absence of air. MaS-1 gave a firm gum, insoluble in THF. MaS-3 gave a soft gum, which was swelled severely by THF, although it failed to dissolve. MaS-5 gave a colorless liquid, presumably a solution of polymerized MAPS in monomeric MPMS. A 50% solution of the liquid in THF was mixed with a small amount of water and a trace of HCl. The aqueous phase slowly dissolved to give a colorless solution. A sample was baked at 150°C for 15 mins to give a colorless, soft film, insoluble in THF. A second preparation, on a larger scale, gave a soft gel in the first step. It was dissolved in MOE by vigorous stirring, but the addition of very dilute HCl to the solution gave an intractable gel.

These experiments were done with commercial MAPS, without any special precautions to exclude moisture. Undoubtedly some siloxane crosslinking occurred, together with the desired vinyl polymerization, during the first stage of the reaction. When a large amount of difunctional MPMS was present, it competed with MAPS for the water present and also cocondensed with the MAPS to give a low degree of crosslinking, and a soluble polymer. More work needs to be done to determine suitable conditions for preparing and curing polymers of this type. However, because of the difficulties outlined above, as well as the unsatisfactory laminating characteristics reported in a subsequent section, it was decided that the time available could be used to better advantage with other polymer systems.

Properties of Neat Polymers

TGA. - Thermogravimetric analyses (TGA) of neat specimens of selected resins were made, using a Perkin-Elmer TGS-2 Thermogravimetric System. Samples of about 5 mg were heated to 1,000°C at a rate of 5°C/min in air and in N_2 at flow rates of 100 cc/min. In the first phase of the program a heating rate of 80°C/min was also used, but results at the more rapid rate did not provide enough additional information to justify their continued determination.

TGA results are given in Table VII. Some conclusions can be drawn from the data, although the generality of the observations is somewhat questionable. The highest absolute char yields were found for the phenolic silicone PS-2 and the PMR polyimide silicone IS-1 in N_2. A substantial part of the residue in these cases was carbonaceous, since it weighed more than the calculated weight of SiO_2. In air the carbon apparently burned completely to give residue weights approximately equal to the expected SiO_2 yield for these materials. Almost all of the silazane epoxies (EpS-22 to EpS-31) gave char yields in N_2 that were about 2-5 times

TABLE VII - THERMOGRAVIMETRIC ANALYSES OF SILICONE MODIFIED POLYMERS AT 5°C/MIN

		Residual Char at 1,000°C, %(1)		Ratio, Av. Char/Calc. SiO_2	
ID No.	Calc. SiO_2, %	Air	N_2	Air	N_2
EpS-8	23.7	21.1 (23.0)	33.1 (40.2)	0.93	1.55
EpS-9	42.8	(37.8)	(42.1)	0.88	0.98
EpS-16	22.8	5.1 (5.4)	11.3 (10.6)	0.23	0.48
EpS-17	16.3	6.1 (6.8)	15.0 (19.4)	0.40	1.06
EpS-18	11.8	5.9	12.2	0.50	1.03
EpS-22	12.9	9.2	24.9	0.71	1.93
EpS-23	4.4	3.5	21.3	0.80	4.84
EpS-24	5.7	4.7	17.7	0.82	3.11
EpS-27	5.3	4.4	23.0	0.83	4.34
EpS-28	4.1	3.9	17.8	0.95	4.34
EpS-29	9.5	8.2	26.9	0.86	2.83
EpS-30	5.7	6.0	25.8	1.05	4.53
EpS-31	7.3	6.5	21.5	0.89	2.95
EpS-32	28.8	24.7	27.4	0.86	0.95
EpS-33	31.5	27.4	31.9	0.87	1.01
EpS-34	4.5	2.6	22.2	0.58	4.93
EpIS-3E	11.3	10.3	41.9	0.91	3.71
EpIS-5	24.8	22.7	49.9	0.92	2.01
IS-1	34.2	(32.1)	(56.4)	0.94	1.65
MaS-5	42.9	(33.0)	(33.4)	0.77	0.78
PS-2	22.9	(22.6)	(63.1)	0.99	2.76

---

(1) Values in parentheses are earlier determinations, mostly from Ref. 1.

the calculated SiO_2 yields. However, the Si content of these resins was low, so the absolute char yields were not especially high. The char yields in air were fairly close to the calculated SiO_2 yields for all of the polymers except EpS-16, which gave a very low char yield. This was the only polymer in which the Si was present as dimethylsiloxane units. It has been noted before[1] that this structure gives low yields of SiO_2, presumably because of the formation of volatile cyclic siloxanes.

Isothermal Weight Loss. - Weight loss measurements of neat samples of the six resins chosen for laminate studies were made in a forced draft oven at 200°C. The samples weighed about 1.5 g and consisted of broken pieces of resin, about 2 mm thick. They had been cured for 17 hrs at 190°C. Duplicates of each resin were run. The results are summarized in Table VIII and Fig. 4. The PMR polyimide silicone IS-1 was substantially lower than the other materials in both weight loss and rate of weight loss. The other samples showed only small differences in total weight loss. However, after an initial rapid loss the rate of loss was lower for the phenolic silicone PS-2 and the epoxy silazane silicone EpS-31 (derived from monophenyl siloxane silazane and MY) than for the other epoxy silicones.

Second Order Transitions. - Several silicone modified epoxy resins were examined by thermomechanical analysis (TMA) to determine second order transition temperatures (Tg). A Perkin-Elmer TMS-2 apparatus was used in the expansion mode, with a flat probe of 0.140" diameter, zero load, a heating rate of 10°C/min, and a helium atmosphere. The specimens were small pieces having flat, parallel faces. They were cut from larger pieces which had been cured as indicated. The polymers tested and results obtained are summarized in Table IX. The type of behavior observed in

TABLE VIII - ISOTHERMAL WEIGHT LOSS OF NEAT RESINS AT 200°C IN AIR

ID No.	Weight Loss, % 3 Hrs	22 Hrs	47 Hrs	90 Hrs	211 Hrs	261 Hrs	Av. Rate of Loss in Last Period, %/100 Hrs
EpS-17	1.35	3.67	5.10	6.79	10.22	10.99	1.68
EpS-17	1.02	3.19	4.56	6.18	9.64	10.39	
EpS-22	1.64	5.06	6.91	8.75	11.44	11.96	1.14
EpS-22	1.70	4.94	6.76	8.49	11.25	11.75	
EpS-31	1.91	4.78	6.31	7.63	9.58	9.94	0.76
EpS-31	1.80	4.56	5.86	7.03	8.83	9.45	
EpIS-5	1.29	3.64	5.09	7.10	10.54	11.36	1.83
EpIS-5	1.04	3.33	4.91	6.90	10.25	11.07	
IS-1	0.61	2.14	2.97	3.65	4.57	4.79	0.46
IS-1	0.51	1.95	2.75	3.44	4.39	4.61	
PS-2	3.29	7.11	8.34	9.32	11.15	11.53	0.86
PS-2	2.63	6.27	7.29	8.15	9.81	10.20	

TABLE IX - THERMOMECHANICAL ANALYSES

ID No.	Cure, Hr/°C	Thickness, Mils	Expansion Max., °C	Inflection (Tg), °C	α, °C^{-1} x 10^{4} (1)
EpIS-1E(2)	1.5/120 + 16/165	10.4	100	118	2.2
EpS-15(3)	7.5/120 + 16/165	22.7	68	60	1.6
EpS-14(3)	5.5/120 + 16/165	23.1	54	57	1.3
EpIS-2E(4)	0.5/120 + 16/165	21.7	62	50, 300	1.6
EpIS-3E	16/120 + 8/170	15.0	--	170	1.3
EpS-8	24/35 + 24/50 + 24/75 + 24/100	60.6	52	68, 308	0.7
EpS-16	65/90 + 3/170	53.8	57	92, 314	1.0
EpS-17	56/100	49.3	86	92, 315	1.3

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(1) Linear coefficient of thermal expansion, 100-300°C.

(2) Polysiloxane from APS + 2 MPMS reacted with PMDA. Product used to cure E8. (Ref. 1)

(3) Polysiloxane from GPS + 2 MPMS. Cured with PMDA (EpS-14) or BTDA (EpS-15). (Ref. 1)

(4) Polysiloxane from APS + 2 MPMS reacted with PMDA. Product used to cure polysiloxane from GPS + 2 MPMS. (Ref. 1)

most cases is illustrated in Fig. 5. In the initial run, a rapid expansion occurred at about 100°C, followed by contraction. In this case, the final apparent thickness was less than the original, but in most cases it was about the same. After the initial heating to 160°C, the sample was cooled in the apparatus, with the probe in contact with the specimen. A second heating cycle of the same specimen gave the second curve, which shows a contraction starting at about 80°C, followed by expansion starting about 120°C. After heating to 300°C, the same specimen was cooled in the apparatus and run again to give the third curve. In this case a normal expansion curve was obtained, with an inflection indicating a Tg at 118°C. All of the samples except EpIS-3E gave this type of behavior, and all were subjected to the same three heating cycles. The expansion maxima in Table IX are the temperatures at which maxima occurred in the first heating cycle. The inflection temperatures are temperatures at which the coefficient of expansion increased during the third heating cycle. The coefficients of thermal expansion are average values calculated from the third run for the temperature interval 100-300°C.

The reasons for the observed behavior are not entirely clear, but it seems likely that the maxima and minima in the first runs are due primarily to stress relief. In the process of simultaneous cure and solvent removal, stresses are produced in the resin. On subsequent heating, the sample may relieve internal stresses by changing shape. Heating to 300°C and cooling slowly anneals out the stresses and gives a normal curve. Other factors that may be involved are solvent loss, further cure reactions, and thermal degradation. Attempts to determine

Tg by DSC gave erratic results, due, at least in part, to evolution of volatile material from some of the samples.

All of the polymers containing linear siloxane segments gave low Tg values, which are probably associated with motion of the siloxane portion of the molecule. In some cases a much higher value was also observed, which is probably related to movements in the more rigid parts of the molecule. It is of interest that the one polymer (EpIS-3E) that lacks linear siloxane units did not show a maximum expansion in the first heating cycle, and its final Tg value was higher than the low values observed for the other polymers. As shown in Fig. 6, EpIS-3E was subjected to the same three heating cycles as the other samples. An increase in Tg occurred following each cycle, presumably because of further cure.

Unfortunately the inflection points are not very clearly defined. To obtain additional information, a fresh sample of EpIS-2E was run in a penetration mode, using a load of 26 g, a heating rate of 10°C/min, and a probe having a hemispherical tip with a diameter of 0.035". Figure 7 shows the result, together with the curve from the third heating cycle of the expansion determination. A very pronounced penetration occurred at 50°C, which agrees well with the 50°C deflection occurring in the expansion curve and indicates softening of the sample at that temperature. Apparently the higher loading of the penetration run obscured the maximum at 62°C which was observed in the first cycle of the expansion run.

The low Tg values indicate motions of the very flexible siloxane chains at moderate temperatures. The second inflection observed in some cases is probably due to motions of segments of other parts of the polymer molecule. The lowest Tg values were found for polymers (EpS-14, EpS-15, EpIS-2E) derived from GPS. Somewhat higher values occurred in the siloxane-silazane-epoxies EpS-16 and EpS-17. The siloxane-imide-epoxies derived from E8 (EpIS-1E and EpIS-3E) were still higher, and the increased siloxane crosslinking of EpIS-3E gave the highest value of all.

Composites

Graphite Fabric. - As a preliminary test of processing characteristics and laminate properties, 3-6 ply laminates were made from several of the polymers, using Hexcel 3T716 graphite fabric. This material consists of unidirectional graphite fibers held together by glass fibers woven in a direction perpendicular to the graphite. Table X gives laminating conditions and flexural strengths for the composites. The precure conditions were generally chosen on a basis of small scale tests of tack and flow. Press conditions were not varied widely. Most of the laminates had a satisfactory appearance and gave a satisfactory ringing sound when struck by a hard object. Improved properties could probably be achieved by changing press conditions or by using a post cure.

In a siloxane-silazane-epoxy system an increase in flexural strength was observed as the siloxane chain was increased from a disiloxane (EpS-21) to a trisiloxane (EpS-20) to a tetrasiloxane (EpS-19). Further increases in siloxane length, however, gave problems with phase separation.

TABLE X - GRAPHITE FABRIC LAMINATES

Polymer	Precure Time, Min.	Precure Temp., °C	Plies	Press Conditions Time, Min.	Press Conditions Temp., °C	Press Conditions Press, MPa (kpsi)	% Resin	Thickness, mm (mils)	Flexural Strength(1), MPa (kpsi)	Laminate No.
EpS-17	15	160	5	60	200	6.6 (0.96)	51	1.24 (49)	740 (107)	F68-136-1
EpS-17	10	155	5	60	200	6.6 (0.96)	49	1.16 (46)	760 (110)	F68-138-1
EpS-18	10	100	3	60	200(2)	6.6 (0.96)	21	0.48 (19)	830 (120)	F68-62-1
EpS-18	10	150	3	60	200	10.3 (1.5)	46	0.76 (30)	650 (94)	F68-63-1
EpS-19	12	145	3	60	190(2)	6.9 (1.0)	20	0.46 (18)	1,530 (222)	F68-59-1
EpS-19	10	155	3	60	190	6.6 (0.96)	20	0.48 (19)	1,340 (195)	F68-59-2
EpS-20	15	140	3	60	200	6.9 (1.0)	22	0.46 (18)	990 (143)	F68-65-2
EpS-20	10	148	3	60	200(2)	6.9 (1.0)	21	0.48 (19)	1,010 (147)	F68-67-1
EpS-20	15	145	4	60	200(2)	6.9 (1.0)	45	0.94 (37)	810 (118)	F68-75-1
EpS-20	15	148	4	60	200	6.9 (1.0)	37	0.81 (32)	860 (125)	F68-75-2
EpS-21	17	148	4	60	200	6.9 (1.0)	24	0.74 (29)	680 (99)	F68-70-1
EpS-21	17	148	4	60	200(2)	6.9 (1.0)	25	0.74 (29)	740 (107)	F68-71-1
EpS-28	7	155	4	60	200	6.6 (0.96)	21	0.61 (24)	830 (120)	F68-125-1
EpS-28	10	170	4	60	200	6.6 (0.96)	24	0.61 (24)	830 (120)	F68-128-1
EpS-29	5	155	6	60	200	6.6 (0.96)	31	0.94 (37)	280 (40)	F68-132-1
EpS-29	5	165	6	60	200	6.6 (0.96)	33	0.99 (39)	300 (44)	F68-134-1
EpIS-3E	4	65	3	60	180(2)	6.6 (0.96)	45	0.89 (35)	180 (26)	F68-13-1
EpIS-4	6	70	3	60	200(2)	6.6 (0.96)	35	0.79 (31)	420 (61)	F68-17-1
EpIS-4	4	70	3	60	200(2)	6.6 (0.96)	30	0.71 (28)	500 (73)	F68-20-1
EpIS-4E	5	70	3	30	220(2)	6.6 (0.96)	43	0.84 (33)	190 (28)	F68-22-4
EpIS-4E	4	70	3	60	220(2)	6.6 (0.96)	33	0.76 (30)	440 (64)	F68-23-4
EpIS-4E	4	70	3	60	220(2)	6.6 (0.96)	38	0.84 (33)	230 (34)	F68-24-4

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(1) Average of 5-8 specimens. Measurements were made on a modified Dillon tensile tester and are for comparison only.

(2) Prepreg inserted into cold press; pressure applied; heated to temperature shown; held for time shown. Other laminates started hot.

A comparison of EpS-17 with EpS-19 indicates higher strength at an NH/epoxy ratio of 0.75 than at a ratio of 1.5. The optimum ratio is probably closer to the theoretically equivalent ratio of 1, although steric factors often lead to incomplete reaction in amine cured epoxies and a consequent shift in the optimum ratio.[10] Relatively low strengths were observed for the silazane-epoxy EpS-18 and for the polymers derived from DDS (EpS-28 and EpS-29). The siloxane-imide-epoxy polymers tested here gave low strengths, although similar systems of lower siloxane functionality gave promising results in earlier work.[1]

Filament Wound Composites. - Six resins were chosen for complete evaluation in 4" x 4" x 0.1" unidirectional flat laminates from filament wound prepreg. The selections were based in part upon the results of preliminary tests and in part upon the desirability of including a variety of polymer types. Tables XI and XII summarize the laminating conditions employed and the properties observed. Precure conditions were chosen to give flexible prepregs with little or no tack. Laminating conditions were chosen that gave moderate resin flow in the press and hard laminates with a good appearance. In several cases poorly bonded regions were revealed by the C scans, although the laminates appeared to be well bonded. Test specimens were cut only from the areas shown by C scans to be fully bonded. Additional study of precure, laminating, and postcure conditions would be required to obtain a high yield of fully bonded laminates with optimum properties.

The highest strength at 25°C was found for EpS-31, which is an amine cured MY720 epoxy resin containing a crosslinked phenyl siloxane-

TABLE XI - FILAMENT WOUND GRAPHITE FIBER LAMINATES

Polymer ID No.	Laminate No.	Plies	Press Conditions				Thickness		Wt. % Resin
			Temp., °C(1)	Time, Min.(1)	Pressure,(1) MPa	kpsi	mm	Mils	
EpS-17	F69-24-1	11(2)	200	60	10.3	1.5	2.44	96	25.7
EpS-22	F33-102-1	10	250	60	0.7	0.1	2.34	92	27.4
"	F33-102-2	10	250	60	1.7	0.25	2.24	88	29.0
"	F33-102-3	10	250	20	0.7	0.1	2.79	110	37.6
			250	40	10.3	1.5			
"	F69-36-1	10	200	30	0.7	0.1	2.54	100	29.2
			200	30	8.6	1.2			
EpS-31	F69-53-2	10	100	30	0.7	0.1	2.29	90	28.0
			200	30	4.3	0.6			
"	F69-54-1	10	50	10	0.7	0.1	2.36	93	28.1
			200	50	4.3	0.6			
EpIS-5	F69-48-2	10	175	30	4.3	0.6	2.36	93	27.8
			225	30	4.3	0.6			
"	F69-55-1	10	50	10	0.7	0.1			28.2
			200	50	4.3	0.6			
IS-1	F33-96-3	9	200	20	0.7	0.1	2.06	81	27.0
			255	40	4.3	0.6			
"	F33-96-4	9	150	30	4.3	0.6	2.29	90	33.6
			250	60	4.3	0.6			
PS-2	F33-93-1	9	180	60	0.7	0.1	2.67	105	29.5
"	F33-95-2	8	200	60	0.7	0.1	2.29	90	32.0

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(1) Where more than one value is given for the same laminate, conditions were changed while the sample was in the press.

(2) This laminate was made with unsized AS4 fiber. All others were made with AS4W sized fiber.

TABLE XII - PROPERTIES OF FILAMENT WOUND GRAPHITE FIBER LAMINATES

Polymer ID No.	Laminate No.	Density, g/cc		Fiber Volume, %	Void Volume, %	Bonded Area(1), %	Flexural Properties(2)				Interlaminar Shear, MPa (kpsi)(2)	
							Strength, MPa (kpsi)		Modulus, GPa (Mpsi)			
		Laminate	Polymer				25°C	200°C	25°C	200°C	25°C	200°C
EpS-17	F69-24-1	1.52	1.19	65.3	2.8	83	900 ± 50	76 ± 6	82 ± 2	11.5 ± 0.5	52 ± 2	6.7 ± 0.6
							(130 ± 7)	(11 ± 0.8)	(11.9 ± 0.3)	(1.7 ± 0.5)	(7.6 ± 0.3)	(0.97 ± 0.08)
EpS-22	F33-102-1	1.49	1.19	62.5	3.1		824	103	92	15	49.9 ± 0.8	6.8 ± 0.2
							(119.5)	(15)	(13.3)	(2.18)	(7.2 ± 0.1)	(0.98 ± 0.02)
"	F33-102-2					91	1,036	69	106	46		
							(150)	(10)	(15.4)	(6.7)		
"	F33-102-3					93	405	25.4	72	2.1		
							(59)	(3.7)	(10.5)	(0.3)		
"	F69-36-1	1.46	1.19	59.8	4.3	99	814 ± 14	88 ± 13	76 ± 1	7.4 ± 0.7	51.2 ± 0.5	7.41 ± 0.05
							(118 ± 2)	(13 ± 2)	(11.0 ± 0.1)	(1.1 ± 0.1)	(7.43 ± 0.07)	(1.075 ± 0.007)
EpS-31	F69-53-2	1.53	1.20	63.7	0.7	98	1,160 ± 10	223 ± 8	105 ± 1	32 ± 3	72 ± 2	13.7 ± 0.8
							(168 ± 1)	(32 ± 1)	(15.2 ± 0.1)	(4.7 ± 0.5)	(10.4 ± 0.3)	(2.0 ± 0.1)
"	F69-54-1					100	1,120 ± 40)	229 ± 12	86 ± 12	27.4 ± 0.4		
							(177 ± 6)	(33 ± 2)	(12.5 ± 1.8)	(3.97 ± 0.06)		
EpIS-5	F69-48-2	1.515	1.28	63.3	3.7	65	583	280	--	41.2	37 ± 2	20 ± 7
							(84.5)	(40.6)	--	(5.98)	(5.3 ± 0.3)	(3 ± 1)
"	F69-55-1					20					19.2	6.0 ± 0.1
											(2.8)	(0.87 ± 0.01)
IS-1	F33-96-3					65	399	55.6	79	10.3		
							(58)	(8.1)	(11.4)	(1.50)		
"	F33-96-4	1.53	1.256	58.7	0.3	90	580 ± 40	69.2 ± 0.6	67 ± 4	7.9 ± 0.3	32 ± 2	3.8 ± 0.3
							(84 ± 6)	(10.0 ± 0.3)	(9.7 ± 0.6)	(1.15 ± 0.04)	(4.6 ± 0.2)	(0.55 ± 0.04)
PS-2	F33-93-1					93	460 ± 120	66 ± 7	65 ± 4	9 ± 4		
							(67 ± 18)	(9.5 ± 1)	(9.4 ± 0.6)	(1.3 ± 0.6)		
"	F33-95-2	1.42	1.155	55.8	4.9	93	150 ± 18	65 ± 12	63 ± 4	17 ± 9	22 ± 2	9.0 ± 0.4
							(22 ± 3)	(9.4 ± 1.7)	(9.1 ± 0.6)	(2.4 ± 1)	(3.2 ± 0.3)	(1.31 ± 0.05)

---

(1) Estimated from ultrasonic C scan. Test samples cut from well bonded areas only.

(2) Single values are from single specimens. Where several specimens from one laminate were tested, values are given as mean ± standard deviation (N = 2-5).

silazane network. The other siloxane-silazane-epoxies, EpS-17 and EpS-22, also had relatively high strength at 25°C. The best retention of strength at 200°C and also the highest absolute strength at 200°C were shown by the anhydride cured siloxane-imide-epoxy EpIS-5. The strength of the EpIS-5 laminate at 25°C was low. However, this laminate contained extensive unbonded areas, and only two flexural strength samples could be obtained from the fully bonded region. Consequently, the values given have a low confidence level. It would be of interest to do additional work to optimize laminating conditions for this polymer.

Weight loss measurements at 200°C were made for the six laminates. The specimens weighed about 0.3 g and were 2-3 mm thick. They were aged in air in a forced draft oven. Results are shown in Table XIII. The weight losses based on the resin portion of the specimens agree reasonably well with the values observed for neat resin specimens (Table VIII). In general, the neat epoxy resins lost a little less weight than the corresponding laminates, while the phenolic was about the same and the neat PMR polyimide was a little higher than the laminate. The PMR polyimide showed substantially less weight loss than the other resins as a composite as well as in the neat state.

TABLE XIII - ISOTHERMAL WEIGHT LOSS OF GRAPHITE FIBER COMPOSITES AT 200°C IN AIR

Polymer ID No.	Weight Loss, %* 7 Hrs	95 Hrs	136 Hrs	200 Hrs	Rate of Loss in Last Period, %/100 Hrs
EpS-17	1.4 (5.4)	2.7 (10.5)	3.1 (12.1)	3.5 (13.6)	0.6
EpS-22	2.3 (7.9)	3.7 (12.7)	4.1 (14.0)	4.5 (15.4)	0.7
EpS-31	1.4 (5.0)	2.8 (10.0)	3.1 (11.1)	3.2 (11.4)	0.2
EpIS-5	1.6 (5.8)	3.3 (11.9)	3.8 (13.7)	4.0 (14.4)	0.3
IS-1	1.1 (3.3)	1.1 (3.3)	1.3 (3.9)	1.3 (3.9)	0
PS-2	2.2 (6.9)	2.7 (8.4)	3.0 (9.4)	3.2 (10.0)	0.3

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*Values in parentheses are based upon the resin present in the composite. The other values are based upon the total weight of the specimen.

EXPERIMENTAL

Siloxane Oligomer Intermediates

G60-4-1. - A solution of 764.5 g (4 moles) of MPCS in 1,000 ml of THF was stirred while a solution of 36.03 g (2 moles) of water in 200 ml of THF was added slowly (1 hr). The THF was then distilled off and the residue was heated to 150°C. A stream of dry nitrogen was passed over the product for 5 hrs as it cooled to room temperature. A little THF was used to rinse the product from the flask to give 684.2 g of solution, a sample of which was titrated with 1.0 N NaOH and found to contain 18.13% Cl. This value corresponds to an average of 3.50 Cl/4 Si, a Cl/Si ratio of 0.875, or 2.29 Si and 2 Cl per molecule.

F69-20-1. - The procedure of G60-4-1 was repeated, using 54.05 g (3 moles) of water. The product weighed 659 g and contained 10.19% Cl (Cl/Si = 0.474; 4.22 Si + 2 Cl per molecule).

G60-17-1. - The procedure of G60-4-1 was repeated, using a solution of 211.6 g (1 mole) of PCS in 500 ml of THF and a solution of 12.00 g (0.667 mole) of water in 100 ml of THF. The product weighed 198.9 g and contained 26.82% Cl (Cl/Si = 1.50; 4 Si + 6 Cl per molecule).

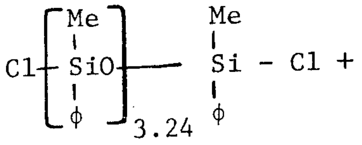
Siloxane oligomers prepared by partial hydrolysis of chlorosilanes were analyzed by titration of the HCl produced when they are completely hydrolyzed. It is assumed that no loss of Si occurs during the synthesis, and so the titration gives the Si/Cl ratio, which can also be expressed as the average chain length for the oligomer. In the titration procedure, a 5 g sample of the product was mixed with 25 ml of THF and 25 ml of 1 N NaOH. This solution was refluxed for 15 mins, cooled, mixed with 25 ml of 1 N HCl, and then titrated with 1 N NaOH to a phenolphthalein endpoint.

To check the validity of the assumptions and the accuracy of the method, a sample of MPCS oligomer F69-20-1 was analyzed by a commercial laboratory (Galbraith). A comparison of results is given on the following page. Agreement between the two analyses was good, and the values obtained for the other elements confirm the composition of the product.

D98-83-9. - A mixture of 296 g (1 mole) of octamethylcyclotetrasiloxane, 129 g (1 mole) of DMCS and 0.09 g of $FeCl_3$ was held at 50°C in a sealed tube for 28 hrs. The liquid was decanted from the solid residue to give 425 g (100% yield) of greenish liquid with a calculated average composition of $Cl[Si(CH_3)_2O]_4Si(CH_3)_2Cl$.

ANALYSES OF F69-20-1

Calc. for 93.34%



$$Cl\left[\begin{array}{c}Me\\|\\SiO\\|\\\phi\end{array}\right]_{3.24}-\begin{array}{c}Me\\|\\Si\\|\\\phi\end{array}-Cl\ +$$

	Galbraith	Titration	6.66% THF
C	56.85	--	57.04
H	5.94	--	5.79
O	8.83	--	9.13
Si	17.58	--	17.57
Cl	10.46	10.19	10.46
Si/Cl	2.12	2.11	2.12

Siloxane-Silazane-Epoxies

EpS-16. - A solution of 8.79 g (0.05 g atom of Cl) of

$$Cl\left[Si(CH_3)_2O\right]_4-Si(CH_3)_2-Cl \quad (D98\text{-}83\text{-}9)$$

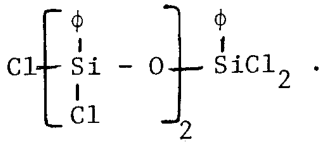
in toluene was stirred while adding a solution of 5.41 g (0.05 mole) of MPD, 10.1 g (0.1 mole) of triethylamine (TEA), 25 ml of toluene, and 25 ml of THF. The mixture was stirred for 15 mins and then filtered. The filtrate was boiled down to 40 ml and mixed with 18.55 g (0.05 mole) of E8. This mixture was evaporated to 34 g and was then baked at 90°C for 65 hrs to give a hard, strong, bubble-free, opaque cake, Shore D75. It was light tan except for a dark brown surface layer. Further baking for 3 hrs at 170°C gave a hard, strong, black cake, Shore D82, free from cracks or bubbles.

EpS-17. - A solution of 108.14 g (1 mole) of MPD, 1,000 ml of THF, and 111 g (1.1 mole) of TEA was stirred while slowly adding a mixture of 23.0 g of G60-4-1 and 307.3 g of F69-20-1. This mixture contained 1 g atom of Cl and 2 g atoms of Si. The mixture was stirred for 30 mins, allowed to stand over night, and filtered. The precipitate was washed twice with THF. The combined filtrate and washings were mixed with 371 g (2 eq. of epoxy) of E8 to give a clear solution weighing about 1,100 g.

EpS-18. - A solution of 21.63 g (0.2 mole) of MPD, 33.33 g (0.33 mole) of TEA, and 100 ml of THF was stirred while adding a solution of 28.67 g (0.15 mole) of MPCS in 150 ml of THF. The mixture became hot and a heavy precipitate formed. After standing over night the mixture was filtered. The precipitate was washed three times with 25 ml portions of THF. The combined filtrate and washings were evaporated in a N_2 stream to 72.77 g and then mixed with 37.1 g (0.1 mole) of E8. A 28.1600 g sample was baked for 66 hrs at 95-100°C to give a black cake weighing 22.4553 g (calc. 19.60 g), Shore D31.

EpS-23. - A solution of 21.16 g (0.1 mole) of PCS in 100 ml of THF was stirred while adding (3 mins) a solution of 120 g (0.0667 mole) of H_2O in 50 ml of THF. The clear, colorless solution was stirred 10 mins and then added (5 mins) to a stirred solution of 33.04 g (0.1667 mole) of MDA in 150 ml of THF. The mixture became warm and a heavy precipitate formed. It was stirred for 10 mins, 33.33 g (0.33 mole) of TEA was added, and stirring was continued for 90 mins. During the addition, more precipitate formed, and the temperature rose. The slurry was filtered. The solid was washed with THF and dried at 85°C in vacuum to give 38.9 g (calc. 41.3 g) of TEA·HCl. The filtrate and washings were combined and evaporated in a N_2 stream. At a residual weight of 52 g the product was a clear amber, viscous liquid. At 51.0 g (calc. 87% solids) it was a waxy semisolid (D98-126-1). A second batch of this intermediate was made by a similar procedure as a 50% solution in THF (F68-101-1). A mixture of 5.10 g (0.05 eq. active H) of D98-126-1 and 9.275 g (0.05 eq. active epoxy) of E8 was an opaque paste at room temperature. When warmed it became clear. At 110°C it set to a clear yellow resin in less than 30 mins. After 66 hrs at 110°C it was clear amber, Shore D85 (D98-127-1). The preparation was repeated, using sufficient THF to give a clear solution at room temperature. This solution was evaporated to a viscous syrup on a hot plate in a stream of N_2. It was then baked under vacuum for 1 hr at 50°C and 2 hrs at 70°C to give a clear, bubble-free viscous liquid. After another hour at 70°C it was a clear solid with large surface bubbles. It was baked further under vacuum at 85°C for 24 hrs. Both this resin and D98-127-1 were baked at 150°C for 48 hrs to give a hard, nearly black product (D98-130-1).

D98-137-2. - A solution of 21.16 g (.1 mole) of PCS in 100 ml of THF was stirred while slowly adding a solution of 1.20 g (0.0667 mole) of H_2O in 50 ml of THF. After 2 hrs at room temperature, the solution was heated in a stream of N_2 until it reached a pot temperature of 55°C and a weight of 16.9 g (calc. 17.5), to give a chlorosiloxane having the average composition



$$Cl\left[\overset{\phi}{\underset{Cl}{Si}} - O\right]_2 \overset{\phi}{Si}Cl_2 \ .$$

It was added slowly to a stirred solution of 33.04 g (0.1667 mole) of MDA, 150 ml of THF, and 20.2 g (0.2 mole) of TEA. The mixture was allowed to stand at room temperature for three days and then was filtered. The filtrate was evaporated in a N_2 stream to a weight of 140.2 g to give a clear orange solution, which was found to contain 31.73% solids. The yield of amine terminated oligomer was 44.50 g (calc. 44.46 g).

EpS-24. - A mixture of 14 g (0.05 eq. NH) of D98-137-2 and 6.1 g (0.05 eq. epoxy) of MY was a clear yellow solution. It was evaporated in a N_2 stream to remove most of the solvent and was then baked under vacuum for 16 hrs at 50°C and 5 hrs at 100°C, followed by 3 hrs at 150°C in air. A clear brown bubbled cake of resin was obtained, Shore D86 (D98-138-5). A second cake was made, using the same quantities, with a cure schedule at atmospheric pressure of 90 hrs at 50°C, 7 hrs at 125°C, and 18 hrs at 150°C. It was brown, cloudy, free from bubbles, Shore D82 (D98-140-1).

EpS-23. - A solution of 14 g of D98-137-2 and 9.28 g (0.05 eq. epoxy) of E8 was cured in the same way as D98-138-5 to give a clear bubbled cake (D98-138-6), Shore D83. A second sample, with the same cure as D98-140-1, was a cloudy, brown, bubble-free cake, Shore D82 (D98-140-2).

D98-139-3. A solution of 24.83 g (0.1 mole) of DDS, 11.2 g (0.11 mole) of TEA, and 75 ml of DMF was stirred while 21.29 g (0.05 mole) of $Cl-[(CH_3)_2SiO]_4-Si(CH_3)_2-Cl$ (D98-83-9) was added slowly. There was an exothermic reaction and a heavy precipitate. The mixture was diluted with 50 ml of THF, boiled for 30 mins, cooled, and filtered. The filtrate was a cloudy yellow liquid (D98-139-3) weighing 111.75 g (calc. 38% solids).

EpS-25. - A mixture was made of 37.25 g (0.1 eq. NH) of D98-139-3 and 12.20 g (0.1 eq. epoxy) of MY. A 1.00 g sample of the cloudy liquid was baked for 96 hrs at 125°C to give a cloudy thick film weighing 0.55 g (calc. 0.53 g), which was flexible and fairly strong. The remainder of the liquid mixture was evaporated in a stream of dry N_2 at room temperature for a week. The residue consisted of an opaque paste and a colorless oil.

EpS-26. - The procedure of EpS-25 was repeated, using 37.25 g of D98-139-3 and 18.55 g (0.1 eq. epoxy) of E8. The cured polymer weighed 0.57 g (calc. 0.53 g). It was opaque, flexible, and strong. It had an oily coating. The residue from evaporation resembled that from EpS-25.

D98-142-1, -2. - A solution of 99.32 g (0.4 mole) of DDS, 44.4 g (0.44 mole) of TEA, and 200 ml of DMF was stirred while 64.58 g 0.4 g atoms Cl) of F68-118-1 was added slowly. THF (200 ml) was added, and the mixture was boiled for 30 mins, cooled, and filtered. The filtrate was evaporated in a stream of N_2 to give a clear yellow solution (D98-142-1) weighing 261.5 g (calc. 45.7% solids). An 8.44 g sample of D98-142-1 was spread in a thin layer and baked for 1 hr at 155°C and 2 hrs at 175°C to give 4.27 g of clear light brown glassy solid (D98-142-2), calc. 90% solids.

F68-118-1. - The first step in the procedure of D98-137-2 was repeated, using 211.6 g (1 mole) of PCS in 500 ml of THF and 12.01 g (0.667 mole) of H_2O in 100 ml of THF. The product was a clear solution weighing 276.0 g. It was found to contain 22.0% Cl (calc. 63.4% solids, 21.4% Cl).

D98-143-5. - The procedure of D98-142-1 was repeated, using 49.66 g (0.2 mole) of DDS, 125 ml of DMF, 44.4 g (0.44 mole) of TEA, and 64.58 g of F68-118-1. In this case, the precipitate that formed contained some gelatinous lumps. An additional 75 ml of DMF and 200 ml of THF was added and the mixture was stirred at high speed in a Waring blender. It was then boiled 30 mins and filtered. The solids were washed twice with 120 ml portions of 2:1 THF/DMF. The insoluble product was stirred with excess water to remove TEA·HCl, filtered, and dried at 110°C in vacuum to give 2.61 g of white powder having an IR spectrum consistent with that of a phenyl siloxane silazane sulfone. The original filtrate and washings were combined and evaporated in a N_2 stream to give a yellow solution weighing 210.7 g.

D98-141-3. - The procedure of D98-141-1 was repeated using 39.65 g (0.2 mole) of MDA, 44.4 g of TEA, 100 ml of THF (in place of DMF), and 64.58 g of F68-118-1. The mixture became very thick and then gelled before the addition was complete.

EpS-27. - D98-142-2 (1.10 g, 0.01 eq. NH) was ground to a powder and mixed with 1.22 g (0.01 eq. epoxy) of MY (preheated to 120°C). The product was baked for 21 hrs at 150°C and 2 hrs at 200°C to give a brown, opaque cake containing darker inclusions, Shore D64. It was not very strong. The procedure was repeated, using 2.18 g (0.01 eq. NH) of D98-142-1 in place of the D98-142-2. The product was similar to that from D98-142-3 but somewhat stronger, Shore D85.

EpS-28. - The procedure of EpS-27 was repeated, substituting 1.86 g (0.01 eq. epoxy) of E8 for the MY. The product was a strong, nearly clear light brown resin, Shore D85. The procedure was repeated, using 2.18 g of D98-142-1 in place of the D98-142-2. The product was similar to that from D98-142-4, with a hardness of Shore D85.

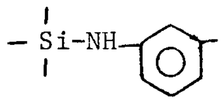
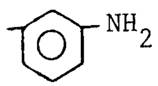
EpS-28. - The remainder of D98-142-1 (244 g, 1.12 eq. active H) was mixed with 207.8 g (1.12 eq. epoxy) of E8 to give a cloudy yellow solution. A sample was baked for 16 hrs at 150°C to give a hard, strong, hazy yellow resin.

EpS-29. - The remainder of D98-143-5 (200 g, 0.38 eq. active H) was mixed with 70.3 g (0.38 eq. epoxy) of E8 to give a cloudy yellow solution. A sample baked for 16 hrs at 150°C was red-brown, opaque, and brittle.

EpS-31. - A solution of 39.65 g (.2 mole) of MDA, 44.4 g (.44 mole) of TEA, and 200 ml of THF was stirred while adding (30 mins) 40.36 g (0.25 g atom Cl) of F68-118-1 (a THF solution of partly hydrolyzed PCS, with 3 Si and 5 Cl per molecule). The mixture was boiled 30 mins, cooled, and filtered. The precipitate was washed three times with THF. Filtrate and washings were combined and evaporated in a nitrogen stream to 122 g to give a clear red solution, which was divided into two equal parts. One part (0.275 eq. active H) was mixed with 33.55 g (0.275 eq. epoxy) of MY to give a clear red solution (calc. 65% solids). A 2 g sample was baked for 94 hrs at 100°C to give a hard, cloudy yellow, intact resin. An additional bake of 16 hrs at 150°C caused darkening but no other change in appearance.

EpS-30. - The other half of the solution prepared in the first part of D98-145-4 was mixed with 51.56 g (0.275 eq. epoxy) of E8 to give a clear red solution (calc. 71% solids). A sample baked out in the same way as D98-145-4 gave similar results.

EpS-34. - A solution of 16.15 g (0.1 mole) of VCS in 100 ml of THF was stirred while adding a solution of 1.20 g (0.0667 mole) of water in 50 ml of THF (5 mins). The resulting solution was evaporated in a nitrogen stream to 50 ml and then added to a stirred solution of 33.04 g (0.1667 mole) of MDA, 20.2 g (0.22 mole) of TEA, and 100 ml of THF. After 15 mins the mixture was filtered. The filtrate was evaporated to 75 g and mixed with 92.75 g (0.25 mole) of E8. The resulting solution was divided into two equal parts. One half was mixed with 0.66 g of TBP. The other half was used without initiator. A 5 g sample of each solution in an aluminum dish was cured in vacuum for 17 hrs at 65°C, and then in air for 2 hrs at 150°C and 3 hrs at 200°C. Both samples gave dark brown, strong resins weighing 3.89 g (calc. 3.94). Both had a Shore D hardness of 84.

Reaction of Aminosilazanes With PMDA. - The procedure of G60-4-1 was used to prepare a THF solution of a linear amine-terminated siloxane silazane from 0.5 mole of MPCS and 0.25 mole of MPD. The solution, D98-130-5, weighed 120.0 g and contained an average of 4 silicon atoms per chain. If we assume that none of the N atoms was bonded to more than one Si atom, the concentrations of  and of  were each 0.00208 mole/g.

A solution of 12.00 g of D98-130-5 (0.025 mole NH_2) and 25 g of DMAC was stirred while PMDA was added in portions. After each addition the viscosity of the solution was determined periodically by drawing it up into a glass tube and measuring the flow time between two marks on the tube. Early in the run the viscosity increased only slightly after each addition, and then stabilized rapidly. Toward the end, small additions of PMDA gave large viscosity increases, and the viscosity continued to increase for many hours after the addition. Under these conditions it was not practical to wait until the viscosity reached its maximum value after each addition, but the next increment was added when the rate of increase had declined to a low level. The results are summarized in Table II.

A series of mixtures was then made, using, in each case, 2.40 g (0.005 mole NH_2) of D98-130-5 and sufficient DMAC to give a final concentration of 30%. A weighed amount of PMDA was added to each sample, and the mixture was stirred until clear (about 5 mins). The resulting solutions were transferred to Gardner tubes, and their viscosities were observed periodically until they became constant. At the concentration and reactant ratios used, constancy was reached in about 2 hrs. Table III and Figure 1 show the amounts used and the results observed.

A sample of the batch with a ratio of 1.03 was baked for 18 hrs at 105°C and 7 hrs at 160°C to give a brown, crumbly solid, which was ground to a powder weighing 1.18 g. The powder was extracted twice with 10 ml portions of heptane. The extract was evaporated to dryness and baked for 15 mins at 140°C to give 0.31 g (54% yield) of a colorless oil having an IR spectrum corresponding to methylphenylpolysiloxane. The residue from the extraction was dried for 15 mins at 140°C to give 0.85 g of yellow powder having an IR spectrum corresponding to an aromatic polyimide.

Siloxane-Epoxies From APS

EpS-8. - A mixture of 22.14 g (0.1 mole) of APS, 36.46 g (0.2 mole) of MPMS, and 6.31 g (0.35 mole) of water was stirred until homogeneous, held at 75°C for 30 mins, and then evaporated at room temperature in a stream of nitrogen for 65 hrs. A viscous, colorless liquid (D98-120-1) was obtained, weighing 41.32 g (108% of weight calc. for complete hydrolysis and condensation). Half of D98-120-1 (0.05 mole NH_2) was mixed with 18.55 g (0.1 mole epoxy) of E8. A 38.00 g portion of the resulting clear liquid was placed in an aluminum pan 6 cm in diameter and cured under vacuum for 24 hrs at 35°C, 24 hrs at 50°C, 24 hrs at 75°C, and 24 hrs at 100°C. The product (D98-122-1) was a clear, light yellow cake about 1 cm thick, flawless except for a few small bubbles, with a hardness of Shore D81 and a weight of 37.93 g (0.2% wt. loss on cure).

EpS-9. - A mixture of 23.63 g (0.1 mole) of GPS, 36.46 g (0.2 mole) of MPMS, 6.31 g (0.35 mole) of water, and 1 drop of conc. HCl was stirred until homogeneous, held at 75°C for 30 mins, and evaporated for 65 hrs at room temperature in a stream of nitrogen. The product was a colorless liquid (D98-120-2) of low viscosity, weighing 47.24 g (107% of weight calc. for complete hydrolysis and condensation). The odor of MPMS was still noticeable above the liquid. This product was mixed with the other half of D98-120-1, and 38.00 g of the resulting clear liquid was cured in the same way as D98-122-1. The cured resin in this case weighed 33.84 g (10.9% loss on cure), had a Shore D hardness of 45, and was badly cracked.

EpS-32. - A mixture of 22.14 g (0.1 mole) of APS, 36.46 g (0.2 mole) of MPMS, and 6.31 g (0.35 mole) of water was stirred until homogeneous, heated for 30 mins at 75°C, and evaporated in a nitrogen stream for 4 hrs to give 45.5 g of a colorless liquid, which was mixed with 24.4 g (0.2 eq. epoxy) of MY. The mixture was not homogeneous, so 7 g of THF was added to give a clear yellow solution (calc. 81.5% solids). Samples in Al dishes were cured in four different ways:

D98-146-1 (22.22 g). Under vacuum 17 hrs at room temperature and 96 hrs at 60°C → 20.16 g (calc. 18.12) clear yellow resin, Shore D72, with cracks and large bubble.

D98-147-5 (22.22 g). Nitrogen blown over surface at room temperature for 17 hrs (clear, viscous, surface skin), followed by 96 hrs at 60°C under vacuum and 16 hrs at 150°C in air → 18.62 (calc. 18.12) clear brown resin, Shore D84, with a few cracks and a large bubble.

D98-147-6 (22.22 g). In air for 17 hrs at 50°C (clear yellow, flawless), 2 hrs at 75°C, 94 hrs at 100°C (clear brown, many cracks), and 16 hrs at 150°C → 18.78 g (calc. 18.12) clear brown resin, Shore D85, with many cracks.

D98-150-3. In air at room temperature for 116 hrs (clear resin, Shore D45), vacuum at 60°C for 185 hrs, and vacuum at 120°C for 24 hrs → clear yellow, flawless resin, Shore D81.

EpS-33. - A mixture of 22.14 g (0.1 mole) of APS, 54.69 g (0.3 mole) of MPMS, and 9 g (0.5 mole) of water was stirred until homogeneous, boiled 10 mins, sparged with nitrogen at 35°C to a weight of 68.5 g, and mixed with 24.4 g (0.2 eq. epoxy) of MY. To get a clear solution (70.7% solids) 15 g of THF was added. Two samples (20.00 g each) in Al dishes were cured as follows: 92 hrs at room temperature in dishes, removed from dishes, 48 hrs at room temperature, 17 hrs in vacuum at 65°C, 4 hrs in vacuum at 90°C, and 140 hrs in vacuum at 120°C → 28.70 g (calc. 28.30) clear, light amber, flawless resin, Shore D84 (D98-151-5).

Siloxane-Imide-Epoxies

D98-117-1. - A solution of 4.43 g (0.02 mole) of APS in 25 ml of THF was stirred while adding 0.18 g (0.01 mole) of water. (The remaining 0.02 mole of water needed for complete siloxane formation is provided by the subsequent imidization reaction.) The solution was refluxed for 15 mins and then added to a refluxing slurry of 4.36 g (0.02 mole) of PMDA in 25 ml of THF. A clear solution was obtained, which was boiled down in a stream of N_2 to 13.37 g (46% solids). An IR spectrum of the solution showed strong anhydride and imide bands at 1,850, 1,780, and 1,720 cm^{-1}, and an amide band at 1,650 cm^{-1}. When the sample on the salt plate was baked for 16 hrs at 100°C, the imide bands (1,780 and 1,720) became stronger, and the anhydride (1,850) and amide (1,650) bands diminished. A further bake of 1 hr at 175°C eliminated the amide band and strengthened both the anhydride and imide bands. A sample of the solution was aged at room temperature with periodic viscosity measurements. The viscosity rose only moderately in about a month (Fig. 2). The solution was cloudy, however, and deposited a small amount of sediment as it aged.

EpIS-3. - A 1.14 g sample of D98-117-1 (1.7 mmoles anhydride) was mixed with 0.37 g (1 mmole) of E8 and part of the resulting solution was applied to a salt plate. The plate was put in a vacuum chamber at 25°C for 16 hrs. The IR spectrum showed strong anhydride and imide bands, amide at 1,630 and an epoxy band at 905 cm^{-1}. A baking schedule of 16 hrs at 100°C, 1 hr at 175°C, and 2 hrs at 225°C eliminated the amide band and weakened the anhydride and epoxy bands, although the latter two were still moderately strong. Imide remained strong. The remainder of the solution was viscous but still fluid after 24 hrs at 25°C. A thin film was baked for 22 hrs at 100°C and 5 hrs at 175°C to give a hard foam.

For comparison, a mixture of 1.86 g (5 mmoles) of E8 and 0.93 g (4.25 mmoles) of PMDA was ground to a paste, applied to a salt plate, and baked for 18 hrs at 175°C and 5 hrs at 275°C. The anhydride and epoxy bands diminished but did not disappear, and a strong ester band developed at 1,740 cm^{-1}.

A second batch of EpIS-3 was prepared, using 4.17 g (18.9 mmoles) of APS, 25 ml THF, and 0.51 g (28.3 mmoles) of water, together with 4.11 g (18.9 mmoles) of PMDA and 25 ml of THF. The solution was boiled down to 15.2 g and was mixed with 4.11 g (11.1 mmoles) of E8. This mixture was boiled down further to 14.8 g (68% solids). A very viscous clear amber liquid was obtained. A 10.5 g sample of the liquid was cured for 1 hr at 85°C in vacuum to give 8.76 g (calc. 7.09 g) of yellow foam, insoluble in DMAC and infusible at 200°C. A second sample (0.41 g) was baked for 45 mins at 95°C and 2 hrs at 170°C to give 0.31 g (calc. 0.28 g) of hard yellow foam.

A larger batch of EpIS-3 was also made. A solution of 66.42 g (0.3 mole) of APS in 450 ml of dry THF was stirred while adding 8.10 g (0.45 mole) of H_2O. The mixture became homogeneous in a few minutes and was allowed to stand an additional 10 mins. It was then added to a boiling mixture of 65.43 g (0.3 mole) of PMDA and 450 ml of dry THF. A clear solution was obtained, which was boiled for 30 mins. It was cooled to room temperature and mixed with 65.46 g (0.176 mole) of E8 to give 259 g of clear solution, viscosity J-K Gardner. A sample of the solution at 25°C increased in viscosity and gelled in about 30 hrs.

EpIS-3E, 4E, 5E. - A series of polymers was made from various combinations of APS, MPS, PMS, PMDA, and E8, using MOE to make a half ester of the anhydride. The procedure was essentially the same as that of EpIS-3 except that excess MOE was added to the solution after the PMDA had been reacted in. This solution was boiled down to a pot temperature of 75°C (30 mins). The E8 was then added and the solution evaporated to 50% solids. The solvent was primarily MOE at this point, with a little residual THF. The compositions prepared are summarized in Table V.

Samples of the seven solutions were put in Gardner tubes and aged at 25°C, with periodic viscosity measurements. The results are shown in Figs. 2 and 3.

Samples of the seven solutions, weighing 2.8 g each, were placed in aluminum dishes 55 mm in diameter and baked as follows: 16 hrs/120°C + 8 hrs/170°C + 3 hrs/200°C + 1 hr/250°C. All samples gave clear yellow bubbled resins after the 120° bake, with only moderate darkening thereafter. The final weight in all cases was 8-11% higher than the weight calculated for complete condensation.

EpIS-4, 4E. - The procedure of EpIS-3 was used with the following ingredients: 44.27 g (0.2 mole) APS, 18.23 g (0.1 mole) MPMS, 14.41 g (0.8 mole) H_2O, 250 ml THF; 43.63 g (0.2 mole) PMDA, 250 ml THF;

43.65 g (0.118 mole) E8. The final solution contained 60.5% solids and had an initial viscosity of I (Gardner), which rose to S in 2 hrs. A second batch was made at 52% solids. The initial viscosity was E. It increased on standing, and the solution gelled in about 3 hrs.

The procedure was repeated except that 25 g of MOE was added to the PMDA-siloxane-THF mixture. This solution was boiled down to 154 g and then mixed with 43.65 g of E8. The resulting 60% solution had an initial viscosity of L, which increased to U in an hour. After 17 hrs the solution had gelled.

Siloxane-Phenolic

PS-2. - A solution of 228.3 g (1 mole) of BPA in 800 ml of THF was stirred while 34 g (2 moles) of anhydrous ammonia was bubbled into the liquid. A mixture of 308.5 g of F69-20-1 (10.19% Cl) and 22.8 g of F69-18-1 (17.60% Cl) was then added over a 30 min period. This mixture of partially hydrolyzed MPCS oligomers contained 1 g atom of Cl and 2 g atoms of Si. The resulting slurry was refluxed for 2 hrs, cooled, and filtered. The filtrate was evaporated to about 800 g by N_2 sparging at 100°C. A warm solution of 40 g (0.285 mole) of HXA in 500 ml of MOE was then added. The resulting solution was evaporated to about 1,000 g.

Siloxane-Imide

IS-1. - A mixture of 400 ml of dry methanol and 80.55 g (0.25 mole) of dried BTDA was refluxed for 1 hr to give a solution of the dimethyl ester. Methyl nadate (98.10 g, 0.5 mole) was then dissolved in the solution, which was allowed to cool to room temperature. Meanwhile a mixture of 221.38 g (1 mole) of APS, 364.60 g (2 moles) of MPMS, and 63.06 g (3.5 moles) of water was stirred for 1 hr to give a clear, colorless solution. The two solutions were mixed and held at about 60°C with nitrogen sparge until the weight reached 833 g. The solution was then diluted to 45% solids with MOE for use in preparing laminates. A small sample of the solution before adding MOE was baked for 16 hrs at 60°C in vacuum to give a foamed solid which was soluble in MOE. A second sample (5.00 g) in an aluminum dish was evaporated at room temperature in a nitrogen stream for 94 hrs and was then baked for 5 hrs at 60°C, 24 hrs at 85°C, 26 hrs at 150°C, and 24 hrs at 225°C. The product was a clear amber, strong resin, Shore D80.

Siloxanes With Vinyl Crosslinking

MaS-1 (D98-147-1). - A mixture of 24.84 g (0.1 mole) of MAPS, 3.6 g (0.2 mole) of water, and 1 drop of conc. HCl was stirred until homogeneous (5 secs). The solution was heated to boiling and then allowed to cool while sparging with nitrogen over night. A colorless liquid was obtained weighing 18.32 g (calc. 17.93). It was mixed with 0.18 g (1%) of TBP and deaerated under vacuum. A 15.2 g sample was placed in an aluminum dish with a second dish floating on the surface to exclude air. It was baked for 5 hrs at 125°C to give a clear, light yellow resin, Shore D92, with many cracks.

MaS-1 (D98-152-3). - A solution of 4.97 g (0.02 mole) of MAPS and 0.05 g of TBP was heated for 1 hr at 155°C to give a colorless, firm gum, which swelled somewhat in THF, but did not dissolve.

MaS-3 (D98-147-2). - The procedure of MaS-1 (D98-147-1) was repeated using 24.84 g (0.1 mole) of MAPS, 9.12 g (0.05 mole) of MPMS, 5.4 g (0.3 mole) of water, and a drop of HCl. The mixture became clear in about 30 secs and gave 25.42 g (calc. 24.74) of colorless liquid, which was mixed with 0.25 g of TBP. A 21 g sample was cured as above to give a clear resin, Shore D90 with many cracks.

MaS-3 (D98-152-2). - A solution of 2.48 g (0.01 mole) of MAPS, 0.91 g (0.005 mole) of MPMS, and 0.03 g of TBP was heated for 1 hr at 155°C in a covered test tube. The product was a colorless, soft gum, which swelled greatly in THF, but did not dissolve.

MaS-5 (D98-149-1). - The procedure of MaS-1 (D98-147-1) was repeated, using 24.84 (0.1 mole) of MAPS, 36.46 g (0.2 mole) of MPMS, 7.2 g (0.4 mole) of water, and a drop of HCl. The sparged liquid weighed 45.90 g (calc. 45.17). It was mixed with 0.46 g of TBP. A 20 g sample in an aluminum dish was vacuum treated, covered, and heated for 23 hrs at 70°C in vacuum. It was still liquid. Baking was continued at 120°C. After 90 mins the sample was hard and cracked. After 5 hrs it was clear, light yellow, cracked, Shore D81.

A sample of the liquid polymer containing TBP was placed in a Gardner tube and aged at room temperature. Initial viscosity was U-V. It rose to V-W in 6 hrs, X-Y in 23 hrs, Z1-Z2 in 48 hrs, and Z2-Z3 in 72 hrs.

MaS-5 (D98-152-1). - A solution of 2.48 g (0.01 mole) of MAPS, 3.65 g (0.02 mole) of MPMS, and 0.06 g of TBP was placed in a test tube, covered with aluminum foil, and heated for 1 hr at 155°C. A clear, colorless liquid was obtained, presumably a solution of polymerized MAPS in monomeric MPMS. A 50% solution of the liquid in THF was mixed with a small amount of water and a trace of HCl. The aqueous phase slowly dissolved to give a colorless solution. A sample was baked at 150°C for 15 mins to give a colorless, soft film, insoluble in THF.

MaS-5 (D98-152-4). - A mixture of 24.8 g (0.1 mole) of MAPS, 36.5 g (0.2 mole) of MPMS, and 0.6 g of TBP was stirred and sparged slowly with nitrogen while it was heated. After 3 hrs at 80-90°C it was a liquid of rather low viscosity. The temperature was increased to 130°C, and a soft gel formed in less than 10 mins. 2-Methoxyethanol (150 ml) was added, and the mixture was stirred rapidly in a Waring blender to give a viscous, homogeneous solution. Water (7.2 g, 0.4 mole) and a drop of concentrated HCl were added, with continued stirring. A soft gel formed.

MaS-10. - The procedure of MaS-1 (D98-147-1) was repeated using 24.84 g (0.1 mole) of MAPS, 29.66 g (0.2 mole) of DMES, 7.2 g (0.4 mole) of water, and a drop of HCl. The sparged liquid weighed 31.36 g (calc. 32.76). It was mixed with 0.31 g of TBP. A 20 g sample was cured as in MaS-5 (D98-149-1). The cured resin had the same appearance, Shore D82.

A sample of the liquid in a Gardner tube at room temperature had the following viscosities: initial C, 3 hrs C-D, 6 hrs D-E, 23 hrs D-E, 72 hrs D-E.

VS-1 (D98-153-4). - A mixture of 19.03 g (0.1 mole of VES, 34.46 g (0.2 mole) MPMS, 7.2 g (0.4 mole) of water, and a drop of concentrated HCl was stirred until homogeneous and then held at 50-60°C in a nitrogen stream for 2 hrs to give a colorless, viscous liquid weighing

36.17 g (calc. 35.16). It was mixed with 0.4 g of TBP. A small sample of the product in an aluminum dish was baked for 3 hrs at 155°C and 24 hrs at 225°C to give a fairly hard resin of rather low strength.

<u>VS-1 (D98-154-1)</u>. - The preparation of D98-153-4 was repeated with double the quantities. The liquid product weighed 74.85 g (calc. 70.32). A 20 g sample was mixed with 0.2 g of TBP and a second 20 g sample was mixed with 0.2 g of dicumyl peroxide. The samples were placed in aluminum dishes, with a second dish floating on the surface to exclude air. They were baked for 16 hrs at 125°C and 6 hrs at 225°C to give soft resins of low strength.

Prepregs and Laminates

As a preliminary, small-scale evaluation, several of the resins were used to impregnate Hexcel style 3T716 graphite fabric. In this fabric, unidirectional graphite fibers are held together by glass fibers running perpendicularly across the graphite fibers. Approximately 5" x 5" sheets were laid on a sheet of Mylar, a small portion of resin solution was added to the sheet, another sheet of Mylar was placed on top, and the resin was worked around with a doctor blade. The sheets were B-staged at the conditions given in Table X. The samples were then cut into 4" x 4" sheets and laminated. The laminating layup included 3-6 sheets of B-staged fabric placed between 2 sheets of heavy aluminum foil which had been sprayed with M/S 122 release agent, and this package placed between 2 steel plates. Laminating conditions are also given in Table X.

Laminates were fabricated on a larger scale from prepreg prepared by filament winding. A McClean-Anderson Model W-1 filament winding machine was set up with a mandrel having a length of 30" and a diameter of 13". The mandrel was covered with Daubert Release Paper 2-65-KG-1. The gears were set up for circumferential winding with an initial band width of 0.15". This means that the head directing the fiber onto the mandrel is moved 0.15" for each revolution of the mandrel. This setting provides for a slight overlapping of the fiber so as to obtain a continuous sheet of impregnated fiber.

The roll of fiber (Hercules AS-4) was placed on a device that allowed it to unroll with a small amount of tension. The fiber strand was threaded through the resin pan, under a 6" dia. roller, out through an adjustable wiper, across a small roller, and then through a guide onto the revolving mandrel. The resin pan, wiper, rollers, etc., are all one unit, which moves in a direction parallel to the axis of the mandrel. The amount of resin build can be varied by adjusting the wiper, but in most cases it was necessary to adjust the viscosity and concentration of the resin solution by the addition of solvent in order to obtain the desired resin content in the prepreg. Solvents which were found suitable for the purpose were THF, DMF, and MOE.

After the mandrel was covered with impregnated fiber, resistance heaters were moved up next to the revolving mandrel. The temperature of the coated fiber was adjusted by placing the heaters at various distances from the mandrel, and was estimated by placing a thermometer close to the mandrel. In general, the operation began at room temperature. The temperature was raised gradually by moving the heaters progressively closer until the desired temperature was reached. The thermal conditions in this step were not well defined, and the primary criterion of suitable precure was the physical state of the prepreg (tack, flexibility, coherence, etc.). When the prepreg approached a tack-free state, it was cut from the mandrel and pressed into fairly flat pieces. In some cases additional precure in an oven was given to the cut pieces.

The sheets of prepreg were cut into 4" x 4" squares, stacked with the fibers parallel, and placed in a steel mold to prevent the fibers from being squeezed out at the edges when pressed. The assembly was placed in the press. In some runs the press was preheated to the desired temperature, and the prepreg stack placed in the hot press. In others the press was cold to start with. Pressure was applied, and the temperature raised and held for a suitable time. Laminates were removed from the press and allowed to cool. Processing conditions and properties of laminates are summarized in Tables XI and XII. Flexural strength and modulus were determined in accordance with ASTM D790 and interlaminar shear strength in accordance with ASTM D2344. Resin content of prepregs or laminates was estimated from the formula

$$\%\ \text{resin} = \left(\frac{W_p - 0.0223\,\frac{A_p}{b}}{W_p}\right) \times 100,$$

in which W_p is the weight in g of prepreg or laminate, A_p is the area of the prepreg in sq. in., and b is the filament winding band width in inches. The factor 0.0223 is the weight of the untreated fiber in g/in. Densities of neat resins were determined by ASTM D792-B, and of laminates by ASTM D792-A1. Fiber volume and void volume were calculated from these values, together with weights of graphite and of resin.

CONCLUDING REMARKS

No one polymer was best in all respects. EpS-31 (a highly cross-linked siloxane-silazane-epoxy resin) had good processing characteristics and gave the highest strength at room temperature: 1,220 MPa (177 kpsi) flexural and 72 MPa (10.4 kpsi) interlaminar shear. However, strength at 200°C was only 19% of the value at 25°C.

EpIS-5 was difficult to process, and the conditions used gave laminates of rather poor quality. Consequently, only a few specimens were available for test. Room temperature strengths were low: 583 MPa (84.5 kpsi) flexural and 37 MPa (5.3 kpsi) interlaminar shear. However, the values at 200°C [280 MPa (40.6 kpsi) flexural and 20 MPa (3 kpsi) interlaminar shear] were the highest observed and are about 50% of the 25°C values.

The PMR polyimide IS-1 had less than half the weight loss at 200°C in air of any of the other polymers. Differences among the others were small.

Char yields in air and in nitrogen were considerably higher for EpIS-5, IS-1, and PS-2 (23-32% in air, 50-63% in nitrogen) than for the silazane based polymers (6-9% in air, 15-25% in nitrogen). To a large extent these values reflect differences in Si content among the polymers.

Recent reports[11,12] indicate that the electrical hazard from graphite fibers released during a fire is not as serious as was thought during the early phases of this project. Hence the original purpose of the program does not appear to be of critical importance at this time. However, silicone modified polymers of the types described here may be of value for other reasons or in other applications such as heat shields or fire resistant barriers. The effect of the siloxane structure in reducing modulus and dissipating kinetic energy may be useful in improving the toughness of relatively brittle resins, such as DDS cured MY720. By curing the MY720 with various mixtures of DDS and siloxane amines, such as those used in EpS-17 and EpS-31, the modulus and toughness of the resulting resins can be varied systematically over a considerable range.

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Curve 721990-A

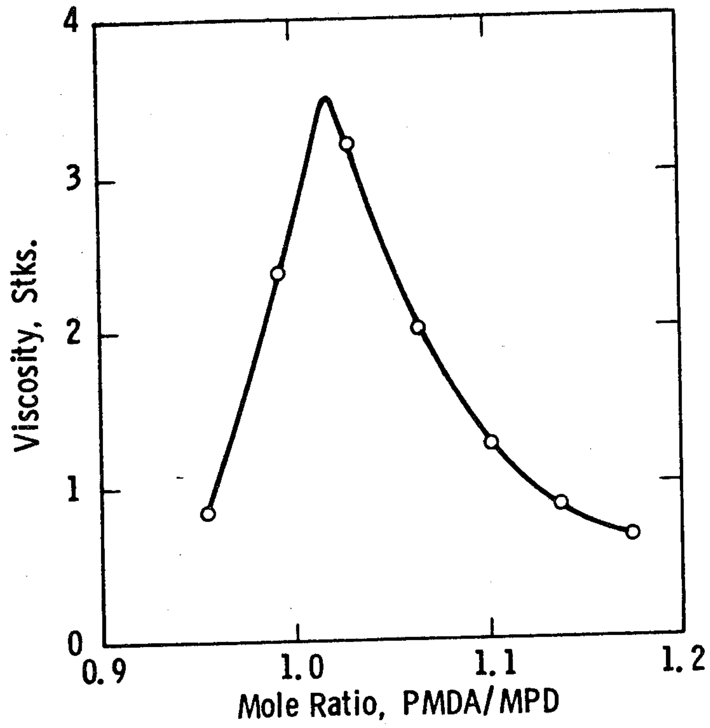

Fig. 1 – Reaction of PMDA and $Mps_4 - Mpd_2$

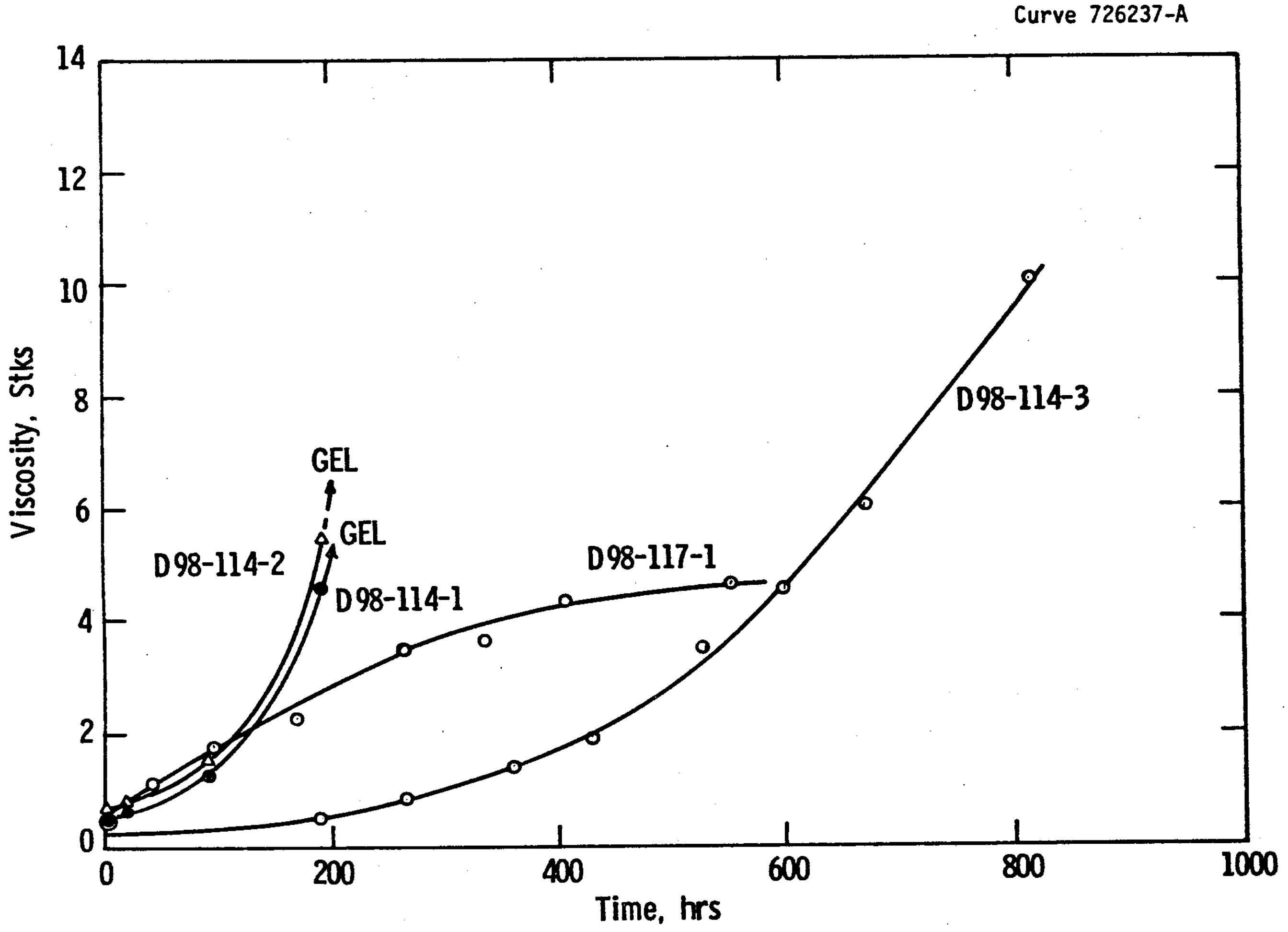

Fig. 2—Shelf life of epoxy silicone precursor solutions at 25°C

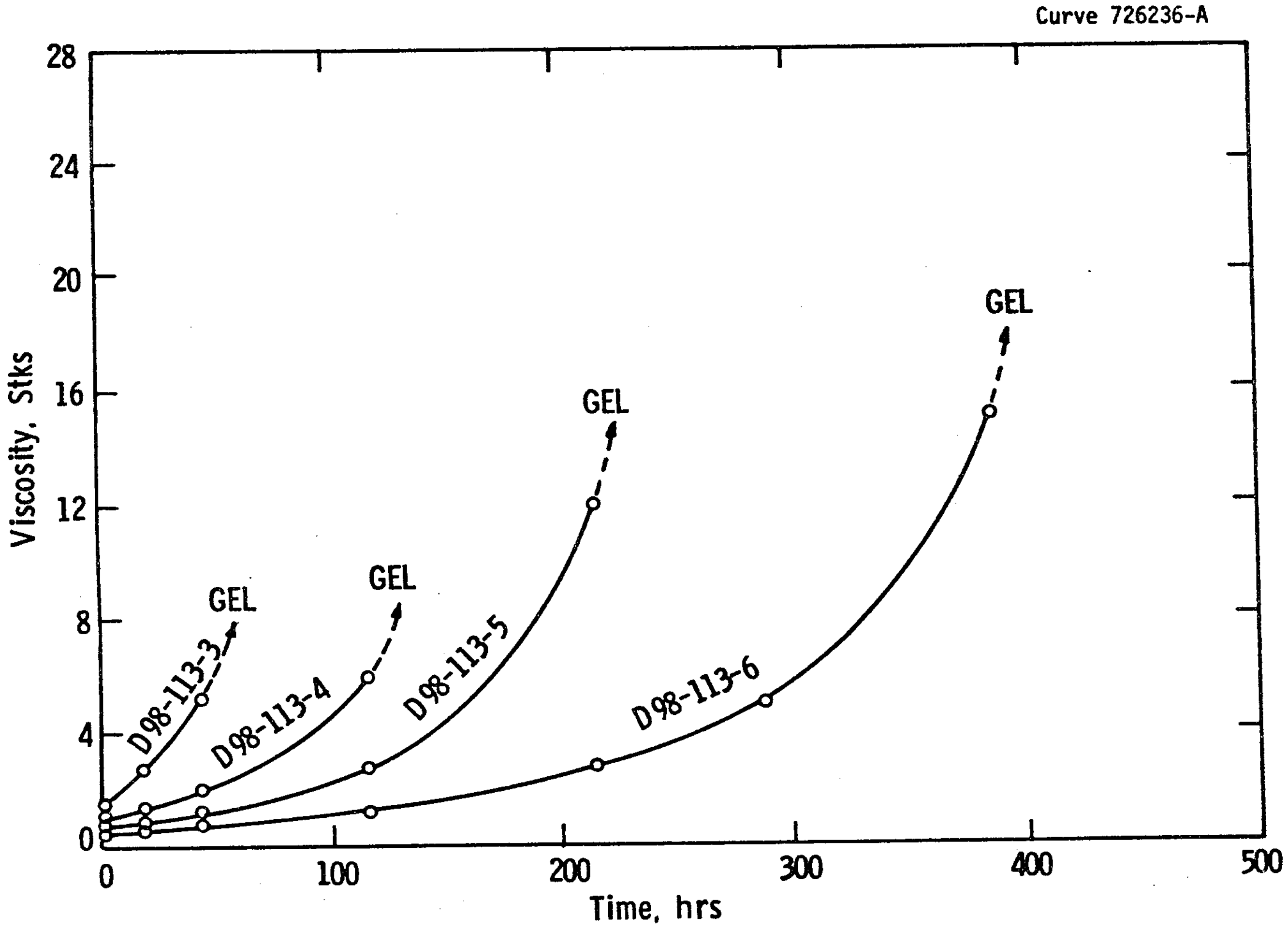

Fig. 3—Shelf life of epoxy silicone precursor solutions at 25°C

Curve 726238-A

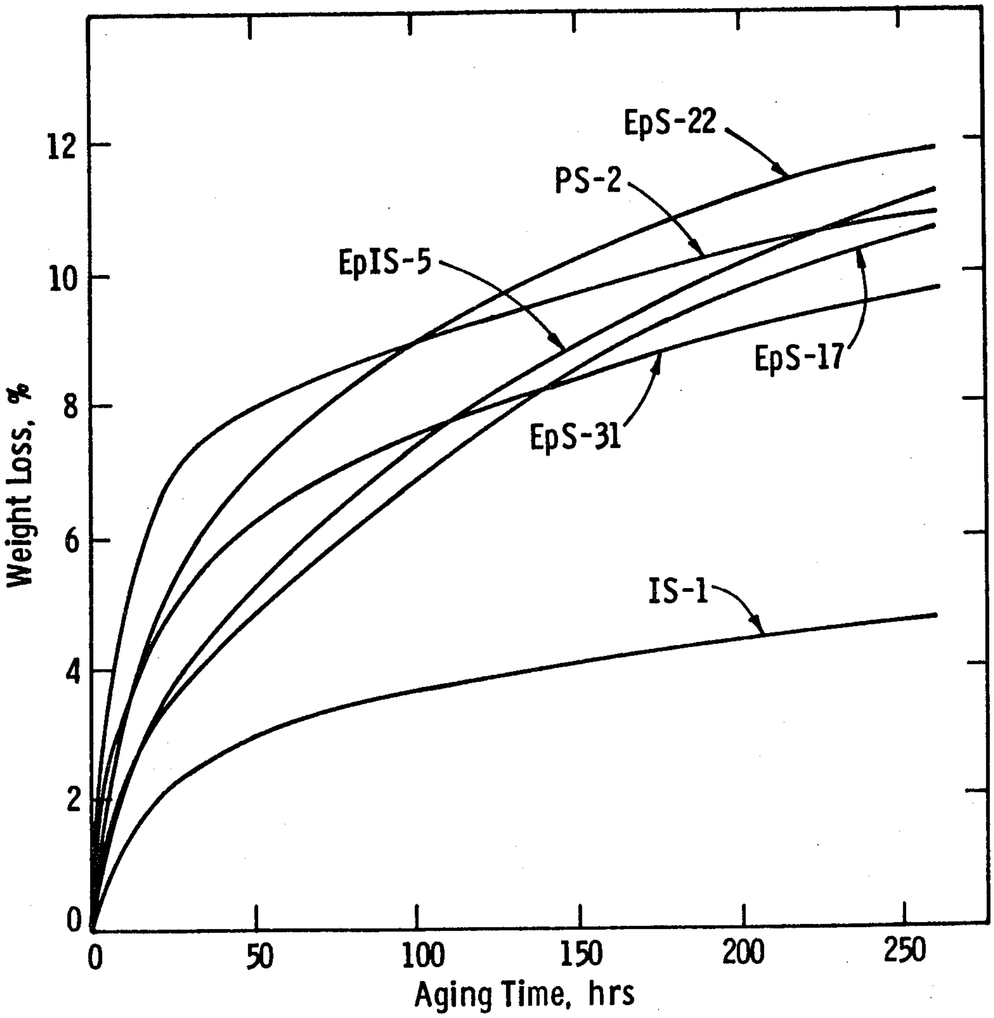

Fig. 4—Isothermal aging of neat resins at 200°C in air

Curve 721737-A

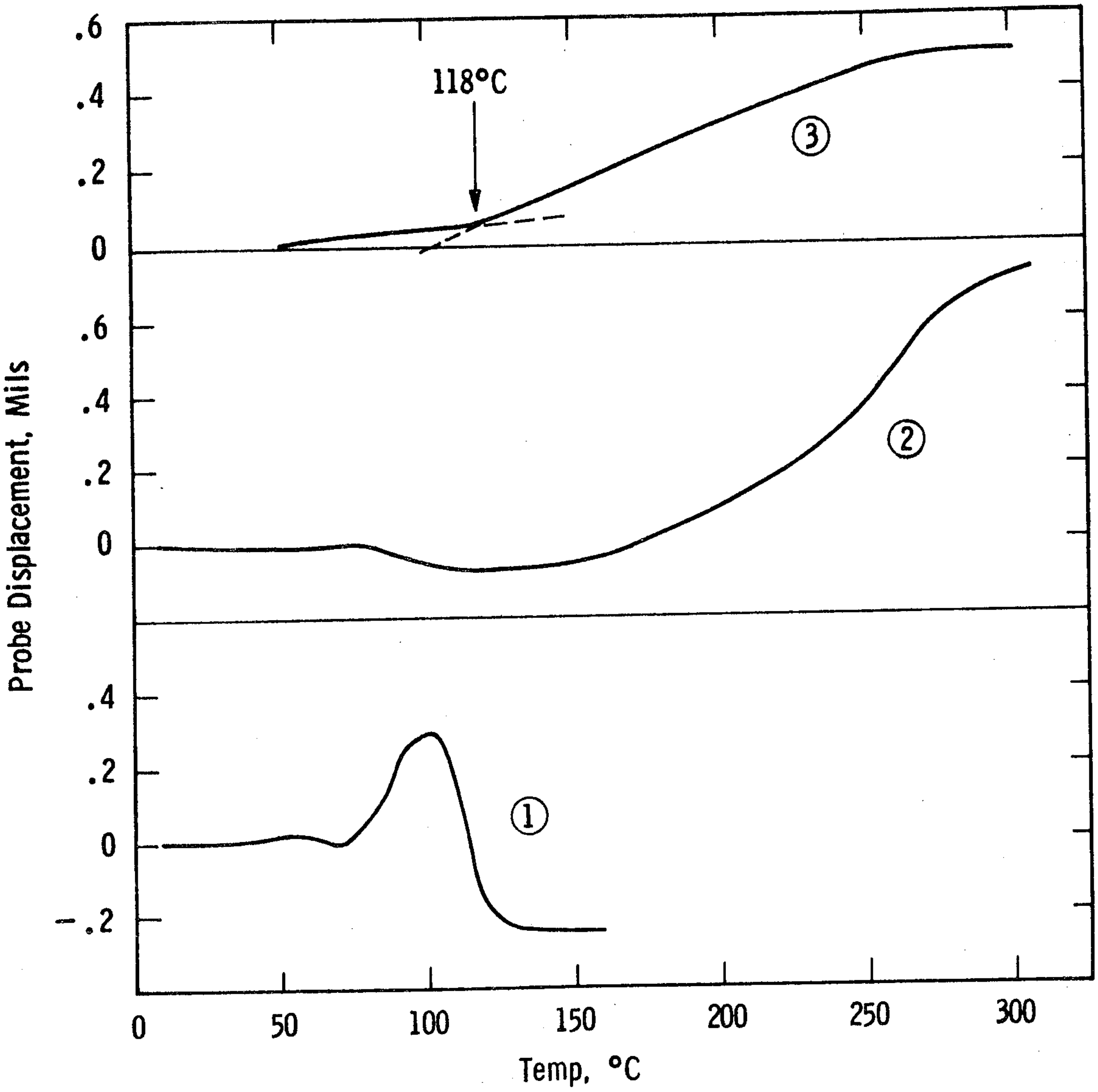

Fig. 5 – TMA of EPIS - 1E

Curve 721738-A

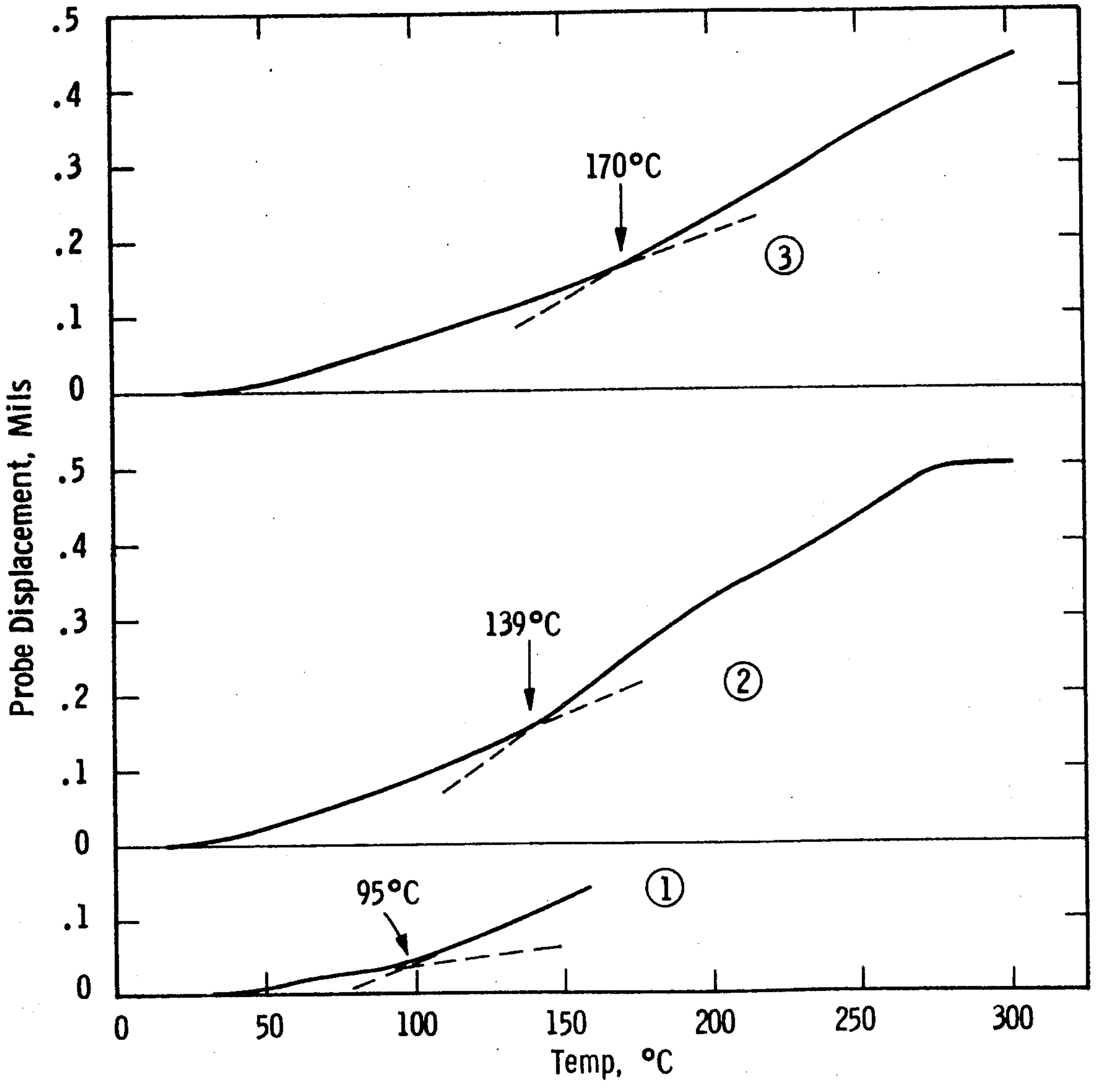

Fig. 6 — TMA of EPIS - 3E

Curve 721736-A

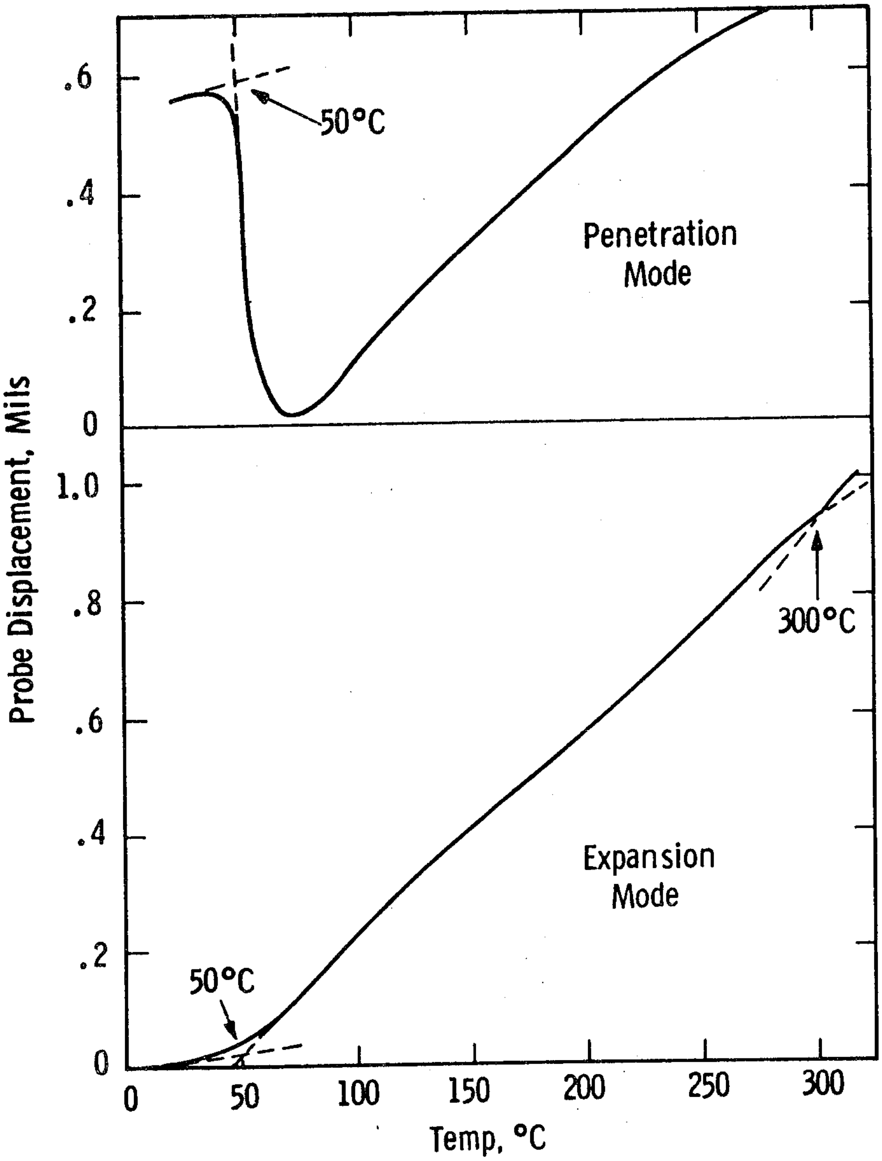

Fig. 7 — TMA of EPIS - 2E

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16. Abstract

When graphite fiber composites are burned, the liberated fibers may settle on electrical apparatus and cause severe damage. This problem can be minimized by bonding the fibers with silicone modified laminating resins that leave a siliceous residual char when they are burned.

During the second year of this program, 23 additional silicone modified resins have been synthesized and evaluated for this application. Included were siloxane-silazane-epoxies, siloxane-imide-epoxies, and unsaturated siloxanes. Further evaluation of resins from the first year was also done. Neat resins were judged in terms of Si content, homogeneity, hardness, char formation, and thermal stability. Char formation was estimated by thermogravimetry to 1,000°C in air and in N_2. Thermal stability was evaluated by isothermal weight loss measurements for 200 hrs in air at 200°C.

Six silicone modified resins were selected for evaluation in unidirectional filament wound graphite laminates. Neat samples of these resins had 1,000°C char residues of 6-63%. The highest flexural values measured for the laminates were a strength of 1,220 MPa (177 kpsi) and a modulus of 105 GPa (15.2 Mpsi). The highest interlaminar shear strength was 72 MPa (10.4 kpsi).

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