Aerospace Research Center

HIGH TEMPERATURE EPOXYCARBORANE ADHESIVES

Contract NAS 9-7001

FINAL REPORT

Dr. Robert Barnes
and
Dr. Edward Hughes

Prepared for:

National Aeronautics and Space Administration
Manned Spacecraft Center
2101 Webster-Seabrook Road
Houston, Texas

June 9, 1968

AEROSPACE RESEARCH CENTER
GENERAL PRECISION SYSTEMS INC
KEARFOTT GROUP
LITTLE FALLS, NEW JERSEY

NASA CR 92327

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Dr. Daniel Grafstein
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ABSTRACT

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Excellent high temperature bond properties have now been demonstrated for bis(epoxybutyl)-carborane cured with a polyfunctional aromatic amine hardener. Lap-shear strengths greater than 1700 psi at 500° F in air have been obtained with steel-on-steel (17/7 specimens). This value represents almost an 85 % retention of room temperature bond strength. Specimens soaked at 500° F in air for 24 hours gave lap-shear strengths of almost 1500 psi at 500° F. These results were obtained on systems which were not optimized in regards to the ratio of reactants and were not modified by fillers, plasticizers or antioxidants. Thus, these systems may reasonably be expected to undergo further improvement in elevated temperature bond strength. Preliminary tests with other carborane derivatives ex. bis(epoxypropyl)carborane and bis(epoxyhexyl)carborane did not give as good high temperature strengths.

This series of bis(epoxyalkyl)carboranes behaves normally with other conventional curing agents. The highest room temperature lap shear strengths obtained on the BF_3:$EtNH_2$ catalyzed system using 17/7 stainless steel adherends are listed below.

	Lap-Shear Strength (psi)
Bis(epoxybutyl)carborane	2320
Bis(epoxypentyl)carborane	2810
Bis(epoxyhexyl)carborane	3600

Because of the superior handling characteristics of the epoxy carborane based adhesives, their ready polymerization under a wide variety of conditions, and the absence of volatile by-products, it is believed that this family of materials offers a viable system for practical high temperature stable bonding requirements.

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ADMINISTRATIVE INFORMATION

This 12 month program was sponsored by the NASA Manned Spacecraft Center, Houston Texas under Contract NAS 9-7001. The NASA Technical Representative was Mr. Ivan K. Spiker/ES4. The Project Supervisor at the Aerospace Research Center, Kearfott Group, General Precision Systems Inc. was Dr. Daniel Grafstein. The Principal Investigator was Dr. Robert Barnes. He was supported by Dr. Edward Hughes who supervised the testing program. Mr. William Benko assisted in the preparation of monomers and Mr. Charles Maccia assisted in the preparation and testing of lap-shear specimens. Gas chromatographic analyses were performed by Mr. Donald Yee. Lap-shear test specimens were machined at the Research Center Model Shop.

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I. INTRODUCTION

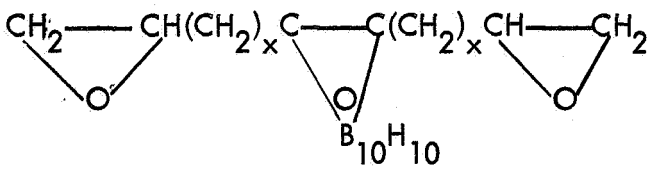
This is the final report on the second year effort of a program [1] to develop epoxyalkyl-carborane adhesives that are stable and useful at temperatures above 500° F. We had previously shown that these epoxy derivatives, when cured with conventional catalysts and reactive hardeners, are excellent room temperature adhesives. The object of the second year of the program was to investigate the high temperature bonding properties of this class of epoxy adhesives.

High temperature stable adhesives are required in space environments for bonding heat shields to spacecraft and for new high speed aircraft such as the SST. The exterior structures of high speed aircraft are heated by air friction and will have to withstand temperatures of 450-500° F for hours at a time during flight and for a minimum of 30,000 hours during the service life of the airplane [2]. Honeycomb sandwich materials are to be extensively used in construction because of the strength and rigidity of these structures for minimal weight of material used. Presently, polyimide is the material used for bonding the honeycomb structure because it is stable at temperatures as high as 500° F and is commercially available. [3] Silicones have been rejected for this application because of their poor strengths. Polybenzimidazoles, although they have superior strength in shorter time periods, have also been rejected because they are not as stable as polyimides when exposed to high temperatures for long periods of time and because they are more difficult to process.

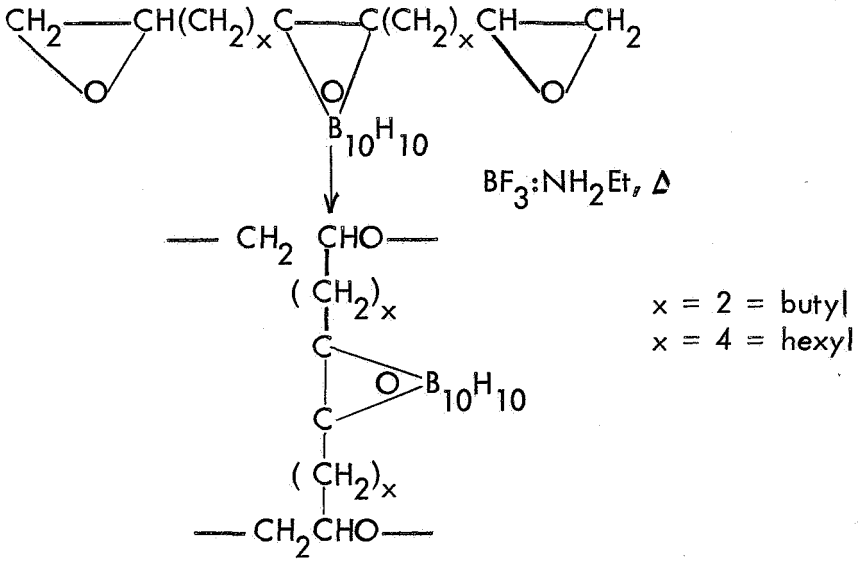
Although polyimides do have attractive strength-temperature relationships, a serious limitation exists in their processability. The mechanism by which the polymer cures to a cross-linked structure with high strength results in the evolution of a volatile by-product, water (i.e. steam). The evolution of volatiles during the cure-assembly cycle gives structures which are poorly formed and are not mechanically acceptable. Some marginal improvement in processing can be made by going to higher bonding pressure. However, this bonding pressure requires extensive modifications in manufacturing equipment and special jigs. In addition, perforated honeycomb must be used for sandwich structures in order to allow the release of volatile curing products. Greater strength-weight ratios are normally obtained with non-perforated structures.

Epoxies are more attractive candidates for adhesive systems than are polyimides. Their advantages are that no volatiles are evolved during the cure cycle (thereby allowing the use of non-perforated honeycomb) and lower temperatures are normally required for cure (as compared to polyimides). However, epoxies which are presently available do not satisfy the high temperature requirements of new aerospace applications. Standard Bisphenol A based epoxy adhesives generally are not useful above 350° F. Some anhydride cured systems, epoxy novolacs and cyclo-aliphatics can be used for short time periods up to 450° F. (4)

Because of the excellent handling characteristics of epoxies and the high order of thermal stability induced by the carborane group to polymer systems, we have undertaken the synthesis and evaluation of a new class of epoxy, the bis(epoxyalkyl)carboranes. (5,6) These materials have the following fundamental structure.



We have previously prepared the terminal diepoxide monomers bis(epoxybutyl)carborane and bis(epoxyhexyl)carborane. (1) Both epoxy derivatives were shown to be easily cured to hard solids at 345° F in the presence of the catalyst boron trifluoride:monoethylamine.



Both epoxyalkyl derivatives can be conveniently "B-staged" at 212° F to give materials which are non-flowing plastics having string-forming characteristics at room temperature. At 212° F, both systems are free-flowing liquids and can be easily applied to metal substrates. Techniques were developed for assembling lap-shear specimens using 17/7 stainless steel. The systems were shown to possess good adhesive qualities and were capable of forming strong bonds to the steel adherend. In the initial adhesive bond evaluation program, room temperature lap-shear strengths up to 2810 psi were achieved on 17/7 stainless steel with the bis(epoxyhexyl)system. The corresponding epoxybutyl system gave values up to 1840 psi. As shown in the following sections, these properties have been significantly improved.

The purpose of the second phase of the program was to evaluate the high-temperature adhesive properties of polyethers formed from bis(epoxyalkyl)carboranes. Structural alternatives were investigated in order to develop an optimum high temperature adhesive system.

Throughout this report, tests on these materials will be designated by a series number which represents the value of x+2. Thus, data on bis(epoxybutyl)carborane is tabulated under the Series 44 designation and data on bis(epoxyhexyl)carborane is tabulated under Series 66.

II. DISCUSSION

A. ADHESIVE BOND EVALUATION

Work performed during this period has shown that bis(epoxybutyl)carborane, when cured with aromatic polyamine hardener G-50, is an excellent steel-on-steel adhesive at 500° F in air atmospheres. This system retains a significant amount of its room-temperature bond strength even after a 24 hour exposure at 500° F. These test results, which are described in the following sections, were obtained on systems which were not modified with fillers or anti-oxidants. The ratio of bisepoxy compound to catalyst or hardener was varied somewhat but the composition has not been optimized. The cure cycles were selected arbitrarily. The adhesive bond properties were determined with conventional lap-shear tests using 17/7 stainless steel adherends. The treatment of the steel surfaces, the structure of the fixture and the method of specimen fabrication are described in the experimental section. Mil Spec MIL-A-005090E was followed in regard to specimen configuration. Results with other curing agents on bis(epoxybutyl)carborane and with other members of the general family of bis(epoxyalkyl)carboranes, while not as encouraging at temperatures above 400° F in air, do demonstrate the versatility of this class of adhesives.

The lap-shear bond strength values reported below are significantly higher than comparable values for several commercially available high temperature epoxy materials. Plastilock 677, a filled epoxy system of proprietary composition, gives lap-shear strengths of 3276 psi at room temperature but only 915 psi at 500° F (time at temperature unspecified - less than 24 hours) [7]. In another system, an epoxy novolac which had been compounded with filler and thixotropic agents, gave room temperature lap-shear strengths of 3,386 psi and a 500° F strength (after being held one-half hour at 500° F) of 1005 psi [8]. The preliminary values already obtained on the bis(epoxybutyl)carborane -amine G-50 system indicates that it should be a better high temperature adhesive than either of the commercially available systems mentioned above. Because this epoxy system has excellent room temperature and high temperature bonding characteristics without the need for filler or antioxidants, an additional program should be undertaken to develop its adhesive bonding technology.

1. Amine G-50 Hardener System

This aromatic polyamine hardener was chosen for evaluation because of its expected high temperature stability and its ability to form highly cross linked structures.

a. Bis(epoxybutyl)carborane

Lap-shear strengths as high as 1730 psi at 500° F were obtained in air atmospheres using a hardener concentration of 47 phr. In a typical preparation (Series 44-19, Table XVI) a mixture of hardener and epoxy was B-staged for 40 minutes at 300° F to give a cloudy viscous liquid. This mixture was then spread uniformly on the overlap areas of the lap-shear specimens. Before final specimen assembly, the epoxy on the strips was outgassed at 0.1 mm and 212° F for 15-20 minutes. A open weave of glass cloth (S-112-38, 220 Volan A finish) was used as a carrier in the overlap area. Specimens were assembled at 390° F for 2-1/2 hours at 120 psi in a Carver Press. Although room temperature strengths were satisfactory (2040, 1850, 1950 and 1420) strengths at 500° F (after a 10 minute hold at temperature) were considerably lower (660, 520 and 830 psi). A two hour post-cure at 500° F resulted in a significant improvement in 500° F strength (1730, 970 and 890 psi). The epoxy was dark brown outside the overlap area and slightly yellow inside the overlap area. The value of 1730 psi represents 85% retention of the best room temperature strength obtained in this series.

Another set of specimens (Series 44-20, Table XVII) was assembled in an identical manner at a hardener concentration of 48 phr and all specimens were post-cured at 500° F for two hours. Lap-shear strengths at room temperature (1070-1450 psi) were lower than those in Series 44-19. Strengths at 500° F ranged from 1060-1580 psi and all failures appeared to be cohesive. Two specimens which were given an additional "soak" of 22 hours at 500° F gave lap-shear strengths of 1300 and 1460 psi at 500° F. The epoxy in the overlap area was yellow with some dark brown areas. The epoxy outside the overlap area was almost black.

In a third series, (44-13 Table XII) a lower amount of hardener (29 phr) was incorporated into the system. B-staging and lay-up conditions were similar to those described above except that a press temperature of 445° F was used. None of the specimens were post-cured in this series. Room temperature strengths of 2200 and 2000 psi were obtained. These values compare favorably with the best obtained on this epoxy (2380 psi in the BF_3:$EtNH_2$ system -- see Section 2a following). However, values dropped rapidly at elevated temperatures.

400° F:	1280, 880 psi
450° F:	560, 430, 480 psi
500° F:	470, 220, 250 psi

The object of Series 14-4 (Table XIII) was to try to improve elevated temperature bond strengths by "priming" the surface before final specimen assembly using a solution of B-staged epoxy. Two samples of epoxy and hardener (30 phr) were B-staged. One sample was dissolved in methylene chloride, and the solution was applied to the overlap area with a medicine dropper. The solvent was removed in vacuo at 212° F and the second sample of epoxy was applied in the normal manner. Cure assembly conditions were 445° F and 120 psi for two hours. Room temperature lap-shear strengths for these samples were lower than expected (1060-1840 psi) and all failures were clearly adhesive. However, strengths at 400° F ranged from 1325-1880 psi which represents nearly 100% retention of room temperature bond strengths. These results indicate that additional work should be undertaken to develop the potential of a priming technique for this system. Methyl ethyl ketone should be used as a solvent for this future work since chlorinated solvents are known to degrade adhesive bond properties.

Additional data (Series 44-21, Table XVIII) supports the earlier data that shows good 500° F bond strength is obtained in this system and cure cycle, when a post-cure temperature near that of the test temperature is used. However, room temperature strengths decrease as a result of this post-cure.

b. Bis(epoxybutyl)-neo-carborane

The above results were obtained with derivatives of ortho carborane in which the carbon atoms are adjacent. Two other isomers of carborane exist in which the carbon atoms are non-adjacent. These latter isomers are more thermodynamically stable than the ortho form of carborane and are derived by thermal rearrangement of that species [9,10]. As a result, they are expected to lead to more thermally stable adhesives. Of the other two isomers, the more readily prepared material is neo (or meta) carborane in which the carbon atoms are in positions 1 and 7. Since the carborane polyhedron acts as a bridge between the polyether crosslinks in the cured epoxy, variations in polyhedron orientation might be expected to play an important role in determining adhesive properties. Bis(epoxybutyl)-neo-carborane was evaluated in Series 44N-16 (Table XIV) using a hardener concentration of 28 phr. The mixture was B-staged for 2-1/4 hours at 300° F to give a liquid which was quite fluid. Cure assembly conditions were similar to those used for the orthocarborane series (i.e. - 445° F at 120 psi for two hours). Room temperature lap-shear strengths of 2000 and 1830 psi were satisfactory but strengths deteriorated considerably at 400° F (440 and 580 psi). Values of less than 225 psi were obtained at 500° F. A post-cure of 527° F for two hours resulted in lower room temperature strength (1340 and 1520 psi) and only slight improvement in 400° F strength (920 psi). However, very thin glue lines on these samples might have contributed to low bond strengths. The remaining portion of the epoxy-hardener mixture was B-staged for an additional three hours at 300° F to give a very viscous liquid. Room temperature strengths decreased (1500 and 1000 psi) and there was no improvement in strength at 400° F (510 psi) or 500° F (200 and 180 psi). A second set of specimens (Series 44N-17 Table XV) was assembled to determine the effect of different cure temperatures on lap-shear strength. Cure-assembly temperatures of 445° F and 420° F were compared. There was no significant difference in strength at 400 or 500° F for the two cure temperatures.

These preliminary results do not indicate that neo-carborane derivatives offer any advantage over the ortho derivatives. However, best results in the ortho-carborane system have been obtained using a hardener concentration of about 50 phr. Testing in the neo system should be repeated using this hardener concentration. An attempt should also be made to develop an optimum cure cycle.

c. Bis(epoxyhexyl)carborane

Initial testing (Series 66-12 Table XXX) was undertaken to determine the potential of this epoxy-hardener system. A viscous B-stage sample was obtained after three hours at 300° F whereas only a 45 minute period was required to obtain a melt of the same viscosity in the bis(epoxybutyl) system. Room temperature lap-shear strengths as high as 3200 psi were obtained but strength at 500° F decreased sharply (235 and 200 psi). One specimen which was post-cured at 500° F for two hours gave a strength of only 120 psi. The excess epoxy-hardener mixture was B-staged for an additional hour at 350° F to increase the viscosity of the sample. No improvement in room temperature or elevated temperature properties was observed.

The elevated temperature strength values obtained in this system are considerably lower than values obtained for bis(epoxybutyl)carborane. However, additional testing should be conducted to determine optimum B-stage and cure-assembly conditions.

d. Bis(epoxypropyl)carborane

Preliminary data (Series 33-1 Table II) was obtained with the bis(epoxypropyl)carborane G-50 hardener system. A mixture of resin and hardener (48 phr) could be B-staged as easily as the comparable bis(epoxybutyl)carborane system. Under the same cure-assembly conditions, room temperature strengths as high as 1740 psi were obtained. Strengths at 500° F dropped and ranged from 580 to 960 psi. A post cure of two hours at 500° F resulted in an increase in 500° F strength (1120 to 1400 psi). Although these results are very preliminary, the pattern seems to follow that for the comparable bis(epoxybutyl)-carborane system (i.e. elevated temperature strength increases as a result of post-cure).

Additional testing should be conducted to determine optimum B-staging and cure assembly conditions.

2. Boron Trifluoride:Monoethylamine Catalyzed Systems

In our previous work, we demonstrated that bis(epoxyalkyl)carboranes were good room-temperature adhesives when cured with the catalyst boron trifluoride:monoethylamine.[1] This catalytic curing system was chosen over a reactive hardener in order to minimize the introduction of non-carborane containing species in the epoxy system. Lap-shear bond strengths as high as 1840 psi were obtained with the butyl derivative whereas values as high as 2810 psi were obtained with the hexyl derivative.

Initial efforts in this portion of the adhesive bond evaluation program were designed to improve room-temperature lap-shear strength values in the butyl and hexyl systems. In addition, test data was needed for the bis(epoxypentyl)carborane system in order to complete the series 44, 55, 66. Testing at elevated temperatures was also initiated in order to measure the range of capabilities and limitations of this adhesive system.

a. Room Temperature Tests - BF_3:$EtNH_2$ Catalyzed Systems

In these tests, mixtures of each epoxy and catalyst (3 phr) were B-staged to viscous liquids at 212° F for periods up to one hour. A glass cloth binder (Volan A-181) was placed in the overlap area to hold the epoxy in place. Specimens were cured in a Carver Press at 120 $\pm$ 5 psi at 445° F for one hour in an air atmosphere. Five samples of the bis(epoxybutyl)-carborane system were prepared. Lap-shear strengths ranged from 1900 psi to 2320 psi and adhesive failure was noted on all samples (Series 44-1, Table III). These results represent an increase in strength up to 28% over those obtained during the first year of the program. The epoxy outside the joint was observed to be yellow after cure but in the joint area itself the epoxy remained white. Two lap-shear specimens were prepared using bis(epoxypentyl)carborane and bond strength values of 2740 psi and 2810 psi were obtained. (Series 55-1, Table XXI). Failure in this system was cohesive and a yellowing

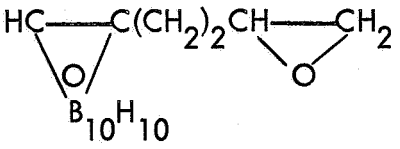
of the epoxy outside the joint area, but not within, was noted. Three specimens of the bis(epoxyhexyl)carborane adhesive gave lap shear bond strengths ranging from 3280 psi to 3600 psi (Series 66-1, Table XXIII). All specimens failed in a cohesive manner. These results show an increase of 28% over bond strength values previously obtained on the hexyl system and represent the highest lap-shear values obtained to date on this program. Color changes in the epoxy were similar to those observed on the butyl and the pentyl systems.

A simple interpretation cannot be offered for the observed trend in lap-shear strengths since adhesive failure was noted for the epoxybutyl system and cohesive failure was noted for the epoxypentyl and epoxyhexyl systems. The change in type of failure is not likely to be due to a surface phenomenon since a standard surface treatment was used on all specimens. In order to explain this change in type of failure, the bond strength between the polyether and the adherend must be greater in the higher alkyl systems than in the butyl system.

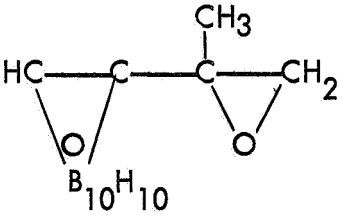
It is felt that an important factor in determining adhesive strength is the interaction of the polyether with the surface of the substrate [11]. One of the factors which affects the magnitude of this interaction is the polar nature of the bonds in the polyether. Introduction of more polar chemical bonds will result in a stronger attraction between the polyether and the substrate, and therefore greater adhesive strength. The inherent polarity of the ether linkage $\overset{+}{C}\text{-}\bar{O}\text{-}\overset{+}{C}$ will be reduced by the presence of the electron withdrawing carborane polyhedron. This reduction in polarity, transmitted through methylene ($-CH_2$) groups, will be greater for the butyl system than the pentyl system. Therefore, the butyl system should give lower adhesive strength, which is consistent with the observed results in the testing program.

The greater lap-shear strength of the hexyl system over the pentyl system however can be related to the cohesive strength of the polyether. [12] This cohesive strength is directly related to the extent of cross-linking in the polymer structure. Based on available chemical evidence, the hexyl system should be more completely reacted than

the pentyl system. The electron-withdrawing carborane cage exerts a deactivating influence on the epoxy ring opening. This effect decreases with increasing distance of the carborane cage from the epoxy ring. For example, the epoxy linkage in epoxybutylcarborane is readily cleaved by acids



whereas, under identical conditions, the epoxy linkage in epoxyisopropylcarborane is stable to attack by acids. (13)



The greater cohesive strength of the hexyl system over the pentyl system can therefore be accounted for if this effect is operative in this system. However, work reported in Section A-1 with amine G-50 suggests that, in this hardener system, the hexyl derivative is less reactive than the butyl derivative. Additional work should be undertaken to investigate this point.

b. Lap-Shear Strength Versus Test Temperature - BF_3:$EtNH_2$ Catalyzed Systems

In this portion of the program lap-shear testing was conducted at several elevated temperatures to determine the nature of the strength versus test temperature relationship. Mixtures of the epoxy and catalyst 3 phr were B-staged for one hour prior to application to the specimens and Volan A-181 glass cloth was placed in the overlap area. The lap-shear specimens were assembled in a Carver Press at 445° F for one hour at a pressure of 120 $\pm$ 5 psi. Several specimens were tested at room temperature to act as controls for each series. The lap-shear strengths obtained in the 44 series (1-6) were averaged and

are listed in Table I. Inconsistent values which were obviously due to poor sample preparation or poor temperature equilibration are omitted. The average lap-shear strengths listed in Table I are plotted as a function of temperature in Figure I. From the data, it can be seen that the epoxy experiences a drastic loss in strength between 350° F and 375° F.

Work described in the following section indicates that oxidation is not the primary cause of bond failure in this system. A physical change in the epoxy in this system could account for the drastic drop in elevated temperature bond strength. However, another explanation is degradation of the BF_3:$EtNH_2$ catalyst and complications derived therefrom. This is consistent with the observation that the G-50 hardener is more thermally stable than BF_3:$EtNH_2$.

c. High Temperature Tests - Air Versus Nitrogen - BF_3:$EtNH_2$ Catalyzed Systems

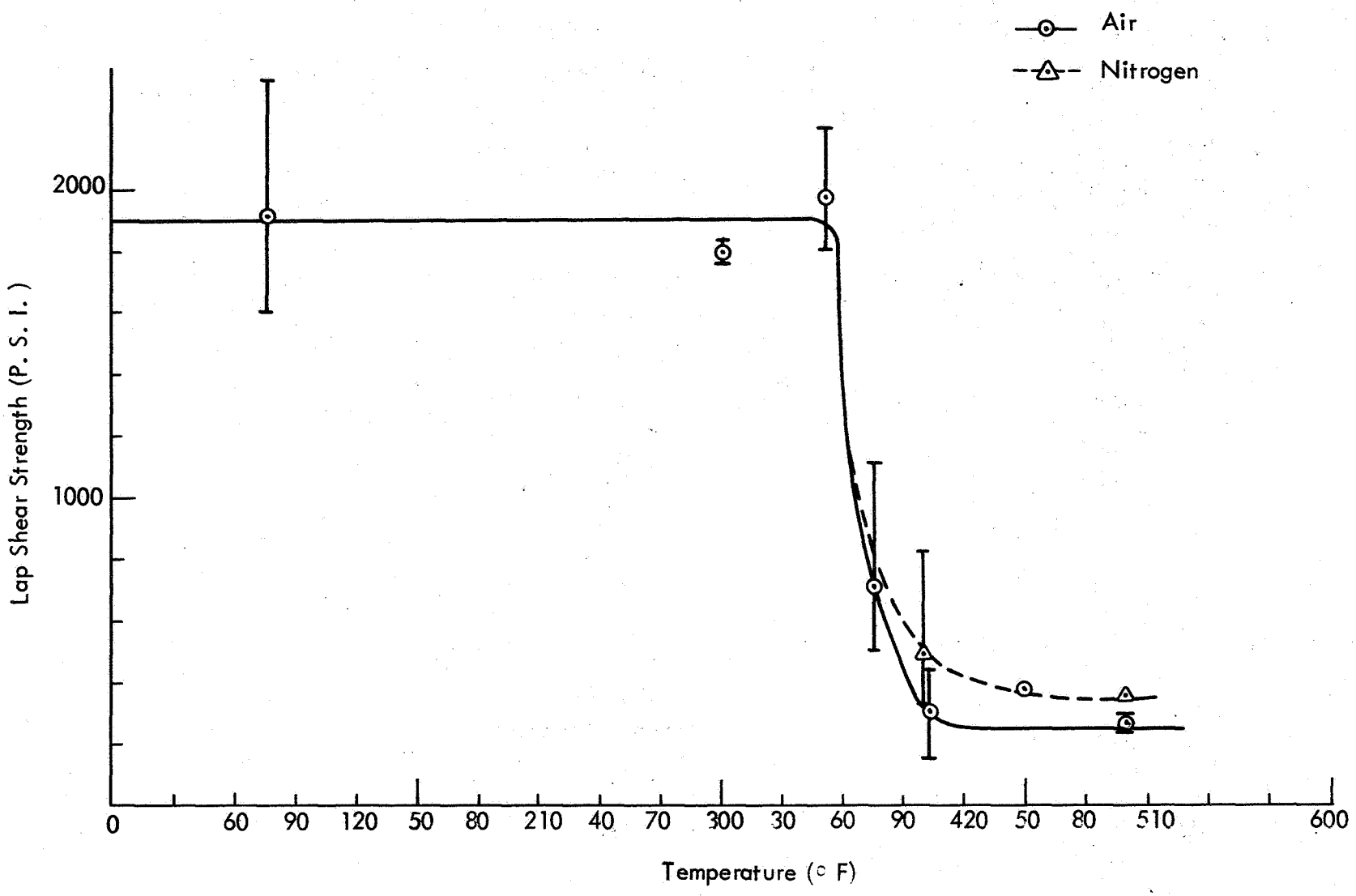
This work was undertaken to determine if the sharp break in the strength versus temperature curve is caused by an oxidative reaction. In Series 44-3 (Table IV) cure assembly conditions were similar to those reported in Section b. Three specimens were tested at room temperature and gave strengths of 2040, 2320 and 2360 psi. Three specimens tested at 500° F in air gave strengths of 238, 290 and 270 psi. The remaining four specimens were tested in a nitrogen atmosphere at 500° F. Lap-shear strengths of 370, 300, 390, and 340 psi were obtained for an increase in average strength of 33% over values obtained in air. Failure mode was mainly adhesive in all tests. The epoxy in the joint area remained white in the nitrogen tests whereas the epoxy turned brown in the air tests. These values are averaged in Table I and are plotted in Figure I along with values at 400° F obtained in nitrogen from Series 44-4 (Table V).

These results indicate that the major cause of bond failure at 500° F is not oxidation of the epoxy system by the air atmosphere. It has independently been shown in this laboratory that degassing the adhesive before testing results in improved room temperature bond strength values. This treatment removed air dissolved in the adhesive. To date, we have not considered the possible oxidation of the epoxy by minute quantities of air dissolved in the system. Future tests in nitrogen atmospheres should be run on samples which have been degassed.

TABLE I

Average Lap-Shear Strength Values
Bis(epoxybutyl)carborane - 3% BF_3:$EtNH_2$

Temperature° F	Average Failure Strength (psi)	Atmosphere	Range (psi)	Number of Values
75	1926	Air	1600-2360	18
300	1795	Air	1790-1800	2
350	1980	Air	1800-2200	3
375	709	Air	500-1120	3
400	320	Air	150-440	5
400	496	Nitrogen	310-820	4
450	390	Air	-	1
500	266	Air	238-290	3
500	350	Nitrogen	360-390	4



LAP SHEAR STRENGTH BIS(EPOXYBUTYL)CARBORANE -3% BF_3:$EtNH_2$

FIGURE I

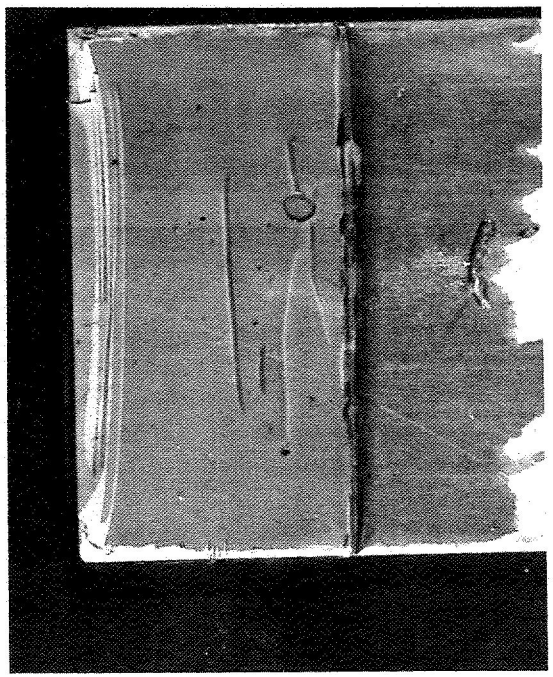
d. Outgassing Studies - Elevated Temperature

A study was made to determine the effect of outgassing prior to cure on room temperature and elevated temperature strength for the butyl system. For Series 44-8 (Table VIII) the epoxy was outgassed at 212° F for 20 minutes at 10^{-2} mm Hg prior to specimen assembly.* Three specimens were tested at room temperature and had values of 1720 psi, 1790 and 1900 psi. Three of the remaining specimens were tested in air at 400° F and three in air at 500° F. The specimens tested at 400° F had values of 720 psi, 950 psi and 980 psi. These values are considerably higher than the values obtained in the 44-5 series previously tested in air at 400° F without prior degassing.

The average strength of 833 psi represents a 43 % retention of room temperature strength as compared to 17 % retention in the previous tests at 400° F (44-5 series). In all three specimens, the failure was adhesive and the epoxy in the overlap area was white. The three specimens tested at 500° F had strengths of 140 psi, 200 psi and 290 psi. The low value of 140 psi was obtained on a specimen which had a large void in the overlap area. These values are comparable to those obtained on earlier specimens from the 44-2 series tested at 500° F in air without prior outgassing. In each case failure was adhesive and the epoxy in the overlap area was slightly discolored.

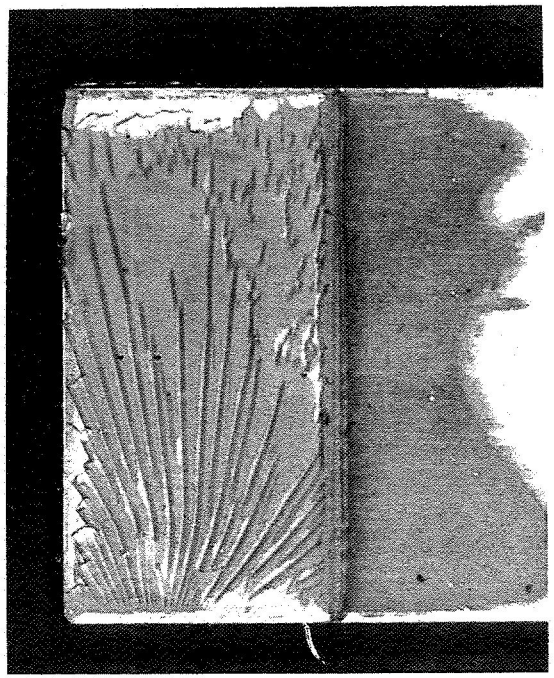
Examination of the fracture surfaces in the 44-8 series reveals an interesting variation in appearance as the test temperature was increased. Typical fractures are shown in Figure II a, b and c. At room temperature (Figure II a) the epoxy remaining on one half of the adherend had a few cracks running across the width of the specimen and almost parallel to the edge. At 400° F, the fracture was characterized by a number of cracks radiating from a nucleus at the edge of the specimen. At 500° F, the fracture appearance was similar to that at 400° F, except that the number of cracks had increased. The reasons for the difference in the type of fracture are not clear at this stage of the investigation.

* Glass cloth was omitted from the overlap area for these tests.



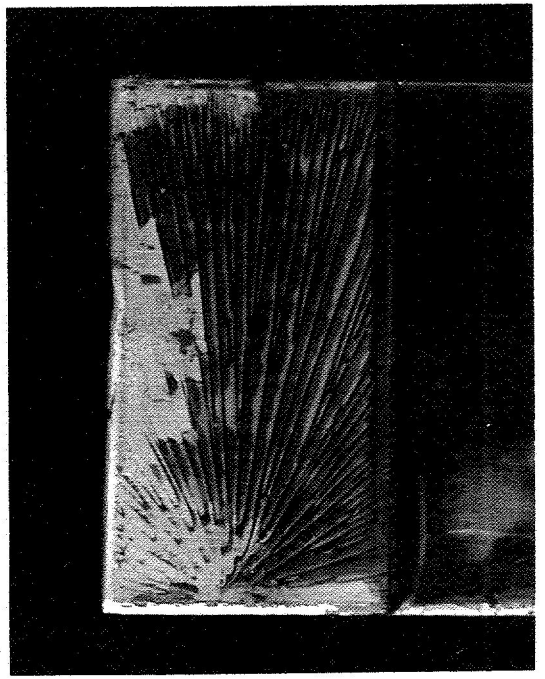
II-a

75° F



II-b

400° F



II-c

500° F

FRACTURE SURFACES
BIS(EPOXYBUTYL)CARBORANE - 3 % BF_3:$EtNH_2$ SYSTEM
OUTGASSING STUDY - 44-8 SERIES

FIGURE II

The changes in lay-up conditions for the 44-8 series (no glass cloth, outgassing and longer B-staging) resulted in a considerable improvement in lap-shear bond strengths at 400° F. Further adjustments in these conditions might result in an improvement in the 500° F strength. For example, the effect on bond strength of the use of glass cloth combined with an outgassing procedure should be investigated.

e. Filler Studies

Skeist [12] suggests that the high coefficient of thermal expansion of unmodified epoxy resins disrupts the adhesive bond with changes in temperature. The thermal coefficients of expansion for an Epon 828 and steel are compared below.

Epon 828, 15 phr metaphenylenediamine	50×10^{-6}/° C
Steel	$8\text{-}12 \times 10^{-6}$/° C

The author states that Sb_2O_3 and aluminum are satisfactory fillers for high temperature adhesives and serve to extend the upper temperature limit.

The coating behavior of cured bis(epoxybutyl)carborane described below indicated that differences in the coefficient of thermal expansion between the epoxy and the steel substrate might be a problem in this work. Samples of the B-staged epoxy (3% boron trifluoride:ethylamine) were applied to three strips of 17-7 stainless steel which had been cleaned and etched in the usual manner. The strips were heated in air at 440° F for one hour. The coatings were tough, clear and off-white in color. One sample was heated at 500° F for one hour. The only observable change was a slight yellowing in color. A second sample was heated at 575° F for one hour. The coating was still tough and hard but darkened considerably and contained several small cracks. No attempt was made to determine if these cracks were present at temperature or if they appeared as the sample cooled. There was no other evidence of degradation. These results suggest that differences in thermal expansion between the polyether and the steel substrate might set up enough stress to cause bond failure in the lap-shear tests.

An investigation was initiated to determine the effect of aluminum filler on elevated temperature strength in the bis(epoxybutyl)carborane - BF_3:$EtNH_2$ system. Two Series of specimens (44-10, Table IX and 44-11 Table X) were assembled using a finely divided grade of aluminum powder available in this laboratory. No attempt was made to pre-treat the aluminum. All bond strengths at 400° F were less than 640 psi. A third series (44-12 Table XI) was prepared using an atomized grade of aluminum powder manufactured by Reynolds Metals Company. There was no improvement in lap-shear strengths at 400° F over values previously obtained. More satisfactory results might be obtained by optimizing the aluminum concentration and cure schedules.

f. Bis(epoxypentyl)carborane at High Temperature

Cure assembly conditions were similar to those reported on the 44 system. Two specimens tested at room temperature gave strengths of 2324 and 2886 psi. However, strengths decreased sharply at 500° F (130 and 240 psi) . (Series 55-2, Table XXII). The epoxy was yellow both inside and outside the joint. No attempt was made to outgas the specimens before assembly. Further work on this system was postponed in favor of work in other areas.

g. Bis(epoxyhexyl)carborane at High Temperature

The lap-shear strength versus temperature curve in the bis(epoxybutyl)carborane - BF_3:$EtNH_2$ system has a sharp break between 350-375° F. Testing was initiated to determine the temperature of the break in the corresponding epoxyhexyl system. Preliminary testing (Series 66-6-10-11) indicates that lap-shear strength rapidly deteriorates above 250° F. Although improvement in bond strength might result from optimizing lay-up conditions and B-staging, additional work was postponed pending results of further testing on other epoxy-hardener systems.

3. Phthalic Anhydride Hardener System

Epoxies cured with anhydride hardeners generally have greater adhesive strength than epoxies cured with catalytic agents. Humphreys attributes this trend to the greater

polarity of the ester linkage (formed by anhydride systems) than the ether linkage (formed by the catalyst system). [14] For this reason, an investigation was initiated to determine assembly conditions for bis(epoxyhexyl)carborane cured with phthalic-anhydride (20 phr) using 1 phr BF_3:$EtNH_2$ initiator (Series 66-3, Table XXV). The system was B-staged at 212° F for four minutes. A preliminary experiment showed that the system could not be outgassed after the B-stage steps because unreacted phthalic anhydride sublimed out of the mixture. Specimens assembled at 400° F and 120 psi without prior outgassing gave lap-shear strengths ranging from 1000-2280 psi. Specimen failures were mainly adhesive and the epoxy inside the overlap area on all specimens but 66-3-10 was yellow. In specimen 66-3-10, which gave the highest lap-shear strength (2280 psi), the epoxy was white in the overlap area. This relationship between high bond strength and color indicates that oxidation occurring during assembly influences bond strength.

Testing was continued in this system to improve bond strength by using a more active catalyst, DMP-30 (Series 66-7, 8 and 9). Room temperature lap-shear strengths as high as 3220 psi were obtained on post-cured systems. However, limited testing at 400° F gave values less than 200 psi. Improvement in these strengths can probably be made by adjustments in the cure cycle and the ratio of reactants.

4. DMP-30 Catalyst System

DMP-30 catalyst was chosen for investigation since this amine is expected to show better thermal stability than BF_3:$EtNH_2$. A mixture of 2.0g of bis(epoxyhexyl)carborane and 0.02g of DMP-30 catalyst was B-staged for one hour at 212° F. Two trays consisting of five lap-shear specimens each were prepared in the usual manner (Series 66-4, Table XXIV). Both sets of specimens were outgassed with the overlap areas exposed for 15 minutes at 212° F under a vacuum of 10^{-2} mm Hg. The first set of specimens was cured in the Carver Press for one hour at 425° F under a pressure of 120 psi. However, no adhesion had occurred and the epoxy was still liquid. The second set of specimens was cured in the Carver Press at a temperature of 575° F for one hour under a pressure of 120 psi. One specimen was defective and not tested.

The remaining four specimens gave strengths ranging from 1150 psi to 1730 psi. All of the failures were cohesive and the epoxy in the overlap area was yellow. Additional testing will have to be conducted to develop satisfactory assembly conditions in this system.

B. PREPARATION OF INTERMEDIATES AND MONOMERS

The synthesis of several terminal bis(epoxyalkyl)carborane monomers required the initial preparation of carborane and the necessary dialkenylcarborane intermediates. First, carborane was synthesized in four steps according to a published reaction sequence. The dialkenylcarboranes were then prepared by the reaction of dilithiocarborane with the appropriate bromoalkene. The reaction of dialkenylcarboranes with trifluoroperacetic acid gave the corresponding bis(epoxyalkyl)carboranes. Last year we reported the preparation of the following compounds by this route:

- 1,2-Bis(3-butenyl)carborane
- 1,2-Bis(5-hexenyl)carborane
- 1,2-Bis(epoxybutyl)carborane
- 1,2-Bis(epoxyhexyl)carborane

Several compounds were prepared and characterized for the first time during the current phase of this program. These are:

- 1,2-Bis(4-pentenyl)carborane
- 1,2-Bis(3-butenyl)-neo-carborane
- 1,2-Bis(2-propenyl)carborane
- 1,2-Bis(epoxypentyl)carborane
- 1,2-Bis(epoxybutyl)-neo-carborane
- 1,2-Bis(epoxypropyl)carborane

The pertinent reaction sequences are summarized below.

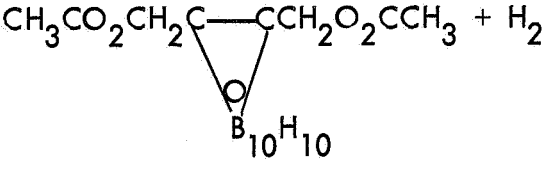
1. Carborane

a. 6,9-Bis(acetonitrilo)decaborane

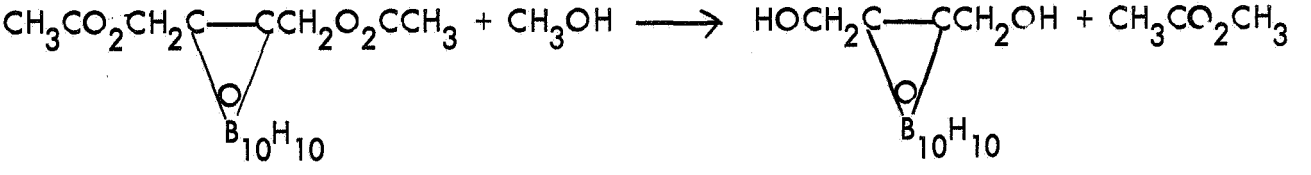
$$B_{10}H_{14} + 2CH_3CN \longrightarrow (CH_3CN)_2B_{10}H_{12} + H_2$$

b. 1,2-Bis(acetoxymethyl)carborane

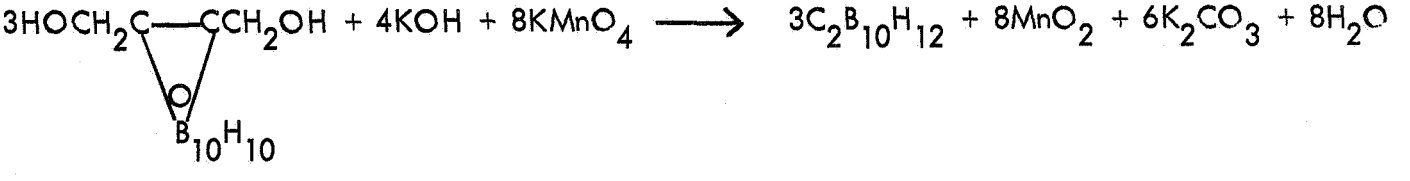
$$CH_3CO_2CH_2C \equiv CCH_2O_2CCH_3 + (CH_3CN)_2B_{10}H_{12} \xrightarrow[\Delta]{\text{Benzene}}$$



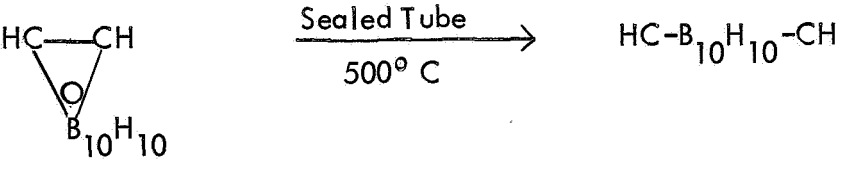
c. 1,2-Bis(hydroxymethyl)carborane



d. Carborane

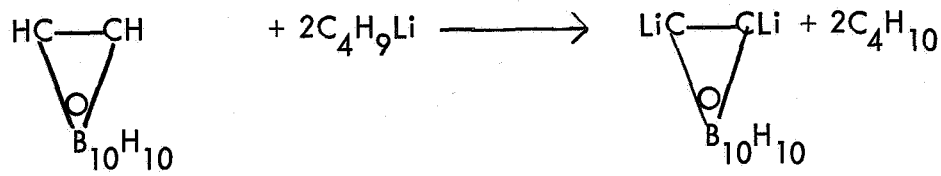


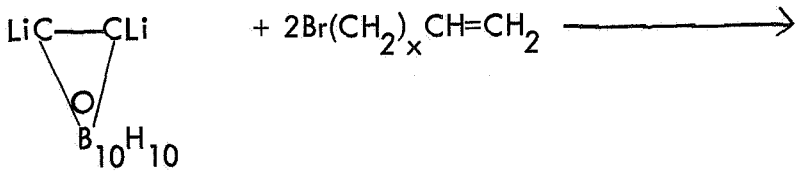
e. Neo-Carborane

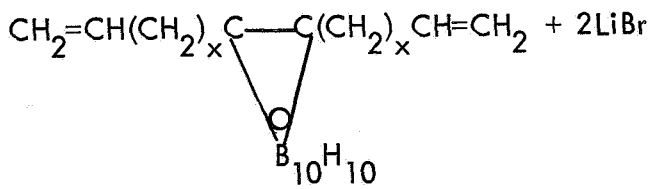


2. 1,2-Bis(alkenyl)carboranes

These compounds were prepared by the following reaction scheme.





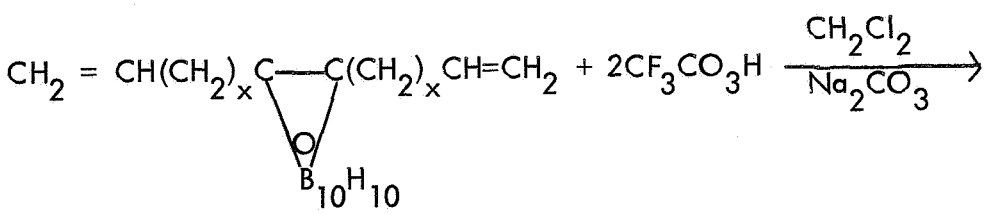


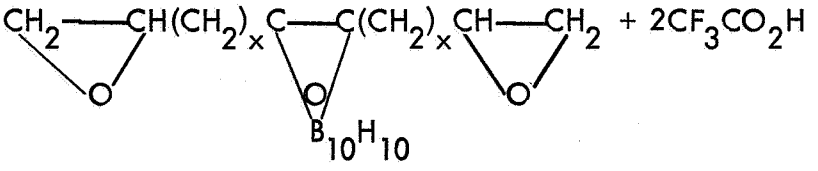
The following compounds were prepared during this investigation.

1,2-bis(2-propenyl)carborane
1,2-bis(3-butenyl)carborane
1,7-bis(3-butenyl)-neo-carborane
1,2-bis(4-pentenyl)carborane
1,2-bis(5-hexenyl)carborane

3. Bis(epoxyalkyl)carboranes

The preparation of these compounds is indicated by the following reaction sequence.





The following terminal bis(epoxyalkyl)carboranes were prepared during this investigation.

1,2-bis(epoxypropyl)carborane
1,2-bis(epoxybutyl)carborane
1,7-bis(epoxybutyl)-neo-carborane
1,2-bis(epoxypentyl)carborane
1,2-bis(epoxyhexyl)carborane

III. EXPERIMENTAL

A. ADHESIVE BOND EVALUATION

1. Preparation of Lap-Shear Specimens and Testing Procedures

Stainless steel strips (17-7) were cut to dimensions called for in Mil Spec MIL-A-005090E (Wep) for lap shear specimens (5.094 in 1.000 in x 0.050 in). All the edges were de-burred. The strips were first degreased in methylethylketone prior to a ten minute immersion in an acid solution at room temperature. This acid solution had the following composition.

Nitric Acid (70 %)	10 %
Hydrofluoric Acid (50 %)	2 %
Water	88 %

On removal from the acid solution, the adherends were thoroughly rinsed with cold water and then immersed in a chromic acid solution for 10 minutes at 160° F. The composition of the acid solution was as follows:

Sodium Dichromate	28.5g
Sulphuric Acid	285g
Tap Water	To make 1 litre
Aluminum Metal	5g

After the acid treatment, the adherends were thoroughly rinsed in cold running tap water. Finally, they were rinsed in distilled water, observed to make sure they held a continuous film of water, and dried in an oven for 30 minutes at 160° F. After the degreasing step, all handling was done using cotton gloves.

The adherends were laid up in a special mounting fixture which ensured accurate alignment of the adherends and an exact overlap of 0.50 in. The fixture could take a total of five specimens (ten adherends). The B-staged epoxy was warmed (212-300° F -- depending on the test sample) and carefully applied to the adherends. The latter were then warmed with an air gun and the liquid was spread over the overlap surfaces. In some cases, the fixture was placed in a vacuum oven at 212° F for 15-20 minutes to outgas dissolved air in the epoxy. A 0.5 inch wide strip of glass cloth (Volan A-181 or 112) was laid over the overlap area of the lower adherend, and the upper adherend was then placed over the

glass cloth. The lay-up fixture containing the specimens was placed in a Carver Hydraulic Press equipped with heating plates and a modified quick closer attachment to ensure constant pressure. After curing, the specimens were removed from the mounting fixture and filed to remove excess epoxy. The glue line thickness in each specimen was determined by measuring the thickness of each adherend adjacent to the overlap area with a micrometer, followed by measuring the total thickness at the overlap area. A simple subtraction gave the glue line thickness. All specimens were tested in an Instron Tensile Tester at a constant strain rate of 0.01 in/in/min. In elevated temperature tests, a specially designed furnace was preheated and placed around the specimen in the Instron Tensile Machine. A period of 15 to 20 minutes was required to bring the specimens to the test temperature. The specimen was held at that temperature for 10 minutes and tested (at temperature).

2. High Temperature Furnace Construction and Calibration

An attachment for the Instron Tensile Machine was constructed which allowed the specimens to be tested at temperatures up to 540° C (1000°F). The attachment was a Nichrome wound tubular resistance furnace which could be quickly mounted in the Instron. The furnace, which had a resistance of 20 ohms, was 7 inches long with an inside tube diameter of 1-1/2 inch. Temperature measurement was made by means of a chromel alumel thermocouple spot welded to the overlap portion of the adherends and positioned according to Mil Spec A-005090E (WEP).

B. SYNTHESIS OF CARBORANE INTERMEDIATES

Procedures for the preparation of the following compounds have been previously described.[1]

- 6,9-Bis(acetonitrilo)decaborane
- 1,2-Bis(acetoxymethyl)carborane
- 1,2-Bis(hydroxymethyl)carborane
- Carborane
- 1,2-Bis(3-butenyl)carborane
- 1,2-Bis(5-hexenyl)carborane

The preparations of those bis(alkenyl)carborane derivatives, which were prepared for the first time during this program, are given below.

1. 1,2-Bis(4-pentenyl)carborane

A slight excess of 1.6M butyllithium solution (125 ml or 0.200 moles of BuLi) was transferred to a dropping funnel in a nitrogen-filled glove bag. The solution was added over a 15 minute period, with stirring, to 11.5g (0.0800 moles) of carborane dissolved in 75 ml of anhydrous ethyl ether. During the addition, a nitrogen flow was maintained over the system, and the flask was cooled with an ice-water bath. After the addition was complete, the suspension of heavy white solid was stirred at room temperature for about one hour. The suspension was allowed to settle, and the bulk of the supernatant liquid was removed with a syringe.

About 75 ml of anhydrous ethyl ether was added to the system with stirring to wash the solid. The bulk of the solution was removed, and the procedure was repeated. About 100 ml of anhydrous ethyl ether was added, and the system was heated to reflux. A weighed quantity of 5-bromo-1-pentene (27.0g - 0.180 moles) was added to the system over a 10 minute period. After a 24 hour reflux period, the reaction mixture was poured into 200 ml of water and thoroughly mixed. The ether layer was separated and dried with magnesium sulphate. A crude product was obtained by evaporation of the ether solvent on a Rinco rotary evaporator. This crude product was separated into several fractions on a vacuum distillation apparatus. The fraction which evolved at a head temperature of 140-150° C was isolated (18g of a colorless liquid -- representing a conversion of 72% carborane to desired product). The infrared spectrum confirmed the formation of the desired material and contained peaks at 3075 cm^{-1} (B-H stretch), 1640 cm^{-1} (C=C stretch), 908 cm^{-1} (CH_2 out-of-plane deformation of the methylene of the $-CH=CH_2$ group) and 725 cm^{-1} (carborane cage vibration). A gas chromatographic analysis indicated that the sample was about 98% pure.

2. 1,7-Bis(3-butenyl)-neo-carborane

A solution of 5.8g (0.040 moles) of neo-carborane dissolved in 75 ml of ethyl ether was added to 50 ml of a 1.6M butyllithium-hexane solution (0.080 moles of BuLi) at 0° C over a 30 minute period. The mixture was heated to reflux and held at that temperature for one hour. Then 10.8g of 4-bromo-1-butene was added to dropwise over a 10 minute period.

The mixture was refluxed for an additional two hours and poured into 200 ml of water. The ether layer was separated, dried with magnesium sulphate, and evaporated on a Rinco Evaporator to constant weight (5.1g of a "wet" solid). A gas chromatographic analysis of this solid indicated the presence of three major components in the ratio 5:1:1. The product was combined with the product of a similar reaction and the bulk was distilled under reduced pressure (0.01 mm). A gas chromatographic analysis of the major fraction which evolved at a head temperature of 150° C indicated a purity of 93 % with the major impurity assumed to be monobutenyl-neo-carborane (6 %). The infrared spectrum of the liquid product contained the following peaks expected for a dialkenylcarborane derivative.

3080 cm^{-1} (C-H stretch of the methylene of the $-CH=CH_2$ group)

1638 cm^{-1} (C=C stretch)

910 cm^{-1} (CH_2 - out-of-plane deformation of the methylene of $-CH=CH_2$ group)

3. 1,2-Bis(2-propenyl)carborane

A solution of 14.4g (0.0100 moles) of carborane was added over a 30 minute period, with stirring, to 150 ml of 1.6M butyllithium solution (0.240 moles of butyllithium). During the addition, a nitrogen flow was maintained over the system and the flask was cooled with an ice-water bath. After addition was complete, the suspension of white solid was stirred at room temperature for one hour. The suspension was allowed to settle, and the bulk of the supernatant liquid removed with a syringe. About 75 ml of anhydrous ethyl ether was added to the system with stirring to wash the solid. The bulk of the solution was removed, and the procedure was repeated. About 100 ml of anhydrous ethyl ether was added, and the system was heated to reflux. A weighed quantity (29g - 0.24 moles) of freshly distilled allyl bromide was added with stirring over a 10 minute period. The mixture turned orange during the addition. After a 24 hour reflux period, the mixture was poured into 200 ml of water and thoroughly mixed. The ether layer was separated and dried with magnesium sulfate. The crude product (19.4g of liquid) was obtained by removal of ether solvent on a rotary evaporator. A gas chromatographic analysis of this

product indicated that it was a complex mixture and contained several major components. In order to isolate a pure sample, a distillation under reduced pressure (8 mm) was attempted on a Podbielniak column. Considerable difficulty was encountered in this distillation because of excessive loss of heat on the pressure drop manometer side-arm, long column warm-up periods and air leakage in the selenoid valve section. The distillation was monitored by gas chromatographic analysis of the fractions. Several fractions were taken off before a single component fraction began to evolve. The distillation was discontinued after a four ml fraction was collected (head temperature of 150-160° C and a pot temperature of 225° C). A gas chromatographic analysis of the fraction indicated it was a single component (99%). The infrared spectrum of the material contained peaks expected for the desired product.

3080 cm^{-1} (CH stretch of the CH_2 of $-CH=CH_2$)
2480 cm^{-1} (BH stretch)
1640 cm^{-1} (C=C stretch)
920 cm^{-1} (CH_2 out-of-plane deformation)
725 cm^{-1} (carborane cage)

C. SYNTHESIS OF BIS(EPOXYALKYL)CARBORANE MONOMERS

The preparation of the following compounds has been previously described.[1]

- Bis(epoxybutyl)carborane
- Bis(epoxyhexyl)carborane

The preparation of those bis(epoxyalkyl)carborane derivatives which were prepared for the first time during this program, are given below.

1. Bis(epoxypentyl)carborane

Trifluoroperacetic acid was prepared in the following manner. Forty ml of methylene chloride was added to 2.2 ml (0.080 moles) of 90% hydrogen peroxide in open beaker cooled by ice water. A total of 11.4 ml (0.080 moles) of trifluoroacetic anhydride was added to the above solution with stirring over a ten minute period. The beaker was

covered with a watch glass, and stirring was continued for another ten minutes. A mixture of 100 ml of methylene chloride, 18.0g of sodium carbonate and 6.5g (0.021 moles) of dipentenylcarborane was placed in a 3-necked round bottom flask. The flask was equipped with a mechanical stirrer, reflux condensor and a dropping funnel. The solution of trifluoroperacetic acid was added dropwise over a 60 minute period. During this time, the temperature of the reaction was maintained below reflux by the use of an ice-water bath. After the addition was completed, the mixture was stirred for 15 minutes at room temperature and refluxed for 90 minutes. Following the reflux period, reaction of a drop of the supernatant liquid to starch-iodide paper was negative, indicating the absence of peroxides. Gravity filtration of the reaction mixture followed by removal of solvent from the filtrate on a rotary evaporator gave a white solid.

The crude product was melted in a vacuum distillation apparatus and distilled. The fraction which evolved at a head temperature of 200-230° C was collected and crystallized. The colorless solid (5g representing a 68 % conversion of carborane to desired product) had a melting point range of 68-75° C. The infrared spectrum contained absorption bands characteristic of the epoxy linkage at 840 cm^{-1}, 860 cm^{-1} and 1260 cm^{-1}. Bands at 1640 cm^{-1} and 3075 cm^{-1} which were present in the infrared spectrum of dipentenyl-carborane had disappeared. Vapor phase chromatography indicated that the purity of the product was about 95 % . An elemental analysis was in excellent agreement with the theoretical values.

Calcd. for $B_{10}C_{12}H_{28}O_2$:	B, 34.6; C, 46.2; H, 9.0
Found:	B, 33.3; C, 45.3; H, 9.1

2. Bis(epoxybutyl)-neo-carborane

Dibutenyl-neo-carborane (6.6g) was treated with trifluoroacetic anhydride and hydrogen peroxide according to the procedures described in (1) above. A cloudy liquid (7.5g) which solidified on standing over a several hour period was obtained. The reaction

was repeated using 5.1g of dibutenyl-neo-carborane and 5.6g of product was obtained. The two crude products were combined and distilled under vacuum (0.05 mm). The fraction which evolved at a head temperature of 140-150° C (pot temperature of 173-180° C) was collected (8.9g). The melting point of this solid was 51-54° C. A gas chromatographic analysis of this fraction indicated the following composition.

bis(epoxybutyl)-neo-carborane - 94.8%
(monoepoxybutyl)butenyl -neo-carborane - 3.6%
dibutenyl-neo-carborane - 1.6%
2 unknowns - trace

The infrared spectrum of the product contained peaks expected for an epoxy derivative (835 cm^{-1}, 855 cm^{-1}, 1250 cm^{-1}, and 3050 cm^{-1}).

3. Bis(epoxypropyl)carborane

The procedure used for the preparation of this compound is described in (1) above. The amounts of reactants were 3.5g of diallylcarborane, 2.2 ml of H_2O_2 and 11.4 ml of trifluoroacetic anhydride. The infrared spectrum of the cloudy liquid product (3.0g) indicated that very little conversion to the epoxy derivative had taken place. The characteristic epoxy bands at 860 and 1250 cm^{-1} were weak whereas the 1640 cm^{-1} band characteristic of unreacted diallylcarborane was strong. The unreacted diallylcarborane (3.0g) which was recovered from this reaction was treated with trifluoroperacetic acid in the presence of 40g of disodium hydrogen phosphate buffer. A gas chromatographic analysis of the product (3.1g -- a cloudy liquid which solidified on standing over a two day period) indicated that the material consisted of a major product (97%) with 2% of a minor component and 1% carborane. The infrared spectrum of the sample is that expected for bis(epoxypropyl)carborane and contained the characteristic epoxy bands at 840, 860 and 1250 cm^{-1}. The diallylcarborane absorption at 1640 cm^{-1} was not present.

IV. FUTURE WORK

Steel-on-steel lap shear strengths of greater than 1700 psi in air have been obtained at 500° F with the system of bis(epoxyalkyl)carboranes cured with conventional coreactants. This represents about an 85 % retention of room-temperature bond strength and demonstrates that the bis(epoxyalkyl)carboranes are superior to presently available adhesives for high temperature applications. Follow-on work is required in several areas in order to satisfy the ultimate goal of determining the adhesive capabilityof the epoxyalkylcarborane systems in bonded joints at elevated temperatures. In the program, which is proposed as a continuation of the present effort, sandwich structures will be fabricated from 17/7 steel honeycomb bonded between steel skins by the epoxycarborane adhesive. The sandwich will be subjected to climbing-drum peel and flexure tests at temperatures from 75° F to greater than 500° F.

The investigation will be divided into three phases.

Phase I - Optimization and Preliminary Evaluation

Several epoxy monomers, previously prepared and characterized in this laboratory, will be optimized to their fullest high temperature potential. Lap shear testing will be conducted to determine optimum resin-curing agent composition of the several available systems. Preliminary testing will be on individual specimens. On the most promising systems, prepunched panels of lap-shear specimens will be assembled and then cut to give individual specimens. Carrier film technology will then be developed for the most promising system.

Phase II - Evaluation of Bis(epoxyalkyl)carborane Adhesives in Honeycomb Panels

The second phase of the proposed effort will be devoted to a complete testing program designed to determine the effectiveness of the particular system developed in Phase I for the adhesive bonding of stainless steel honeycomb sandwiches. Climbing drum peel tests and flexure tests will be conducted. Tests in this phase of the program will be carried out at room temperature (75° F) and 500° F. Initially, the specimens will be

brought to temperature, and held at the test temperature for ten minutes prior to testing. Tests will then be conducted to determine the variation of strength as a function of time at temperature.

Phase III - Development Study

A feasibility study will be undertaken to evaluate the utilization of materials developed under this program for commercial use. The following items will be considered:

availability of raw materials
practicality of monomer synthetic routes for commercial production
potential demand for monomers
potential demand for compounded product.

The epoxy composition which was generated and evaluated (Phase I and II) will be evaluated at temperatures above 500° F. The variation of bond strength with time at temperature will be studied. This evaluation will be conducted with lap-shear tests and honeycomb sandwich specimens.

When the high temperature bonding properties of epoxyalkylcarboranes have been demonstrated in stainless steel honeycomb structures, the following studies should be undertaken.

1. Evaluation of bond strengths for other metal-metal combinations, including aluminum and titanium.
2. A high temperature bond evaluation of nonmetallic honeycomb sandwich panels constructed from a composite material of glass fiber and epoxyalkyl-carborane resin-hardener.
3. A low temperature (-320° F to +75° F) adhesive bond evaluation on lap-shear and honeycomb structures assembled with bis(epoxyalkyl)carborane adhesives.
4. A study of the effects of fuels, solvents and humid environments on the bond strength of assembled structures.

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APPENDIX

Experimental data pertaining to the discussion of lap-shear strength for bis(epoxyalkyl)-carborane adhesives is found in the following Tables. Preliminary work which has not been summarized in this report can be found in the three interim reports. [6]

TABLE II

Lap-Shear Strengths (Series 33-1)
Bis(epoxypropyl)carborane - 48 phr G-50 Hardener

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
33-1-1	75	0.003	1660	cohesive
33-1-2	75	0.003	1670	cohesive
33-1-3	75	0.003	1740	cohesive
33-1-4	75	0.003	1680	cohesive
33-1-5	500	0.003	580	coh-ad
33-1-6	500	0.004	960	cohesive
33-1-7	500	0.003	935	cohesive
33-1-8	500 *	0.003	1120	cohesive
33-1-9	500 *	0.004	1400	cohesive
33-1-10	500 *	0.004	1220	cohesive

* post-cured for 2 hours at 500° F

Composition - 1.52g epoxy + 0.73g hardener
B-stage - 300° F for 40 minutes
Outgassed - yes
Glass Cloth - Style 112
Cure, Assembly - 390° F, 120 psi, 2-1/2 hours
Post-Cure - as indicated

TABLE III

Lap-Shear Strengths (Series 44-1)
Bis(epoxybutyl)carborane - 3 phr BF_3:EtNH_2

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-1-1	75	0.006	2180	adhesive
44-1-2	75	0.005	1900	adhesive
44-1-3	75	0.005	1980	adhesive
44-1-4	75	0.003	2320	adhesive
44-1-5	75	0.003	1940	adhesive

Composition - 1.86g epoxy + 0.06g catalyst
B-stage - 230-265° F for 50 minutes
Outgassed - No
Glass Cloth - Style 181
Cure-Assembly - 445° F, 120 psi, one hour
Post-Cure - None

TABLE IV

Lap-Shear Strengths (Series 44-3)
Bis(epoxybutyl)carborane - 3 phr BF_3:$EtNH_2$

Specimen Number	Test Temperature ° F	Test Atmosphere	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-3-1	75	Air	0.005	2320	adhesive
44-3-2	75	Air	0.003	2040	adhesive
44-3-3	75	Air	0.005	2360	adhesive
44-3-4	500	Air	0.005	238	adhesive *
44-3-5	500	Air	0.009	290	adhesive *
44-3-6	500	Air	0.007	270	adhesive *
44-3-7	485	N_2	0.010	370	adhesive *
44-3-8	500	N_2	0.006	300	adhesive *
44-3-9	500	N_2	0.006	390	adhesive *
44-3-10	500	N_2	0.008	340	adhesive *

* slightly cohesive

Composition - 2.04g epoxy + 0.06g catalyst
B-stage - 212° F for one hour
Outgassed - No
Glass Cloth - Style 181
Cure Assembly - 445° F, 120 psi, one hour
Post-Cure - None

TABLE V

Lap-Shear Strengths (Series 44-4)
Bis(epoxybutyl)carborane - 3 phr BF_3:EtNH_2

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure *
44-4-1	75	0.005	1600	adhesive
44-4-2	75	0.007	1900	adhesive
44-4-3	75	0.008	1790	adhesive
44-4-4	300	0.006	1790	adhesive
44-4-5	300	0.008	1800	adhesive
44-4-6	300	0.007	710 (1)	adhesive
44-4-7	400	0.008	280	adhesive
44-4-8	400	0.007	1790 (2)	adhesive
44-4-9	400	0.007	410	adhesive
44-4-10	450	0.009	390	adhesive

(1) attributed to poor surface preparation
(2) attributed to short equilibration period
* slightly cohesive

Composition - 2.04g epoxy + 0.06g catalyst
B-stage - 212° F for one hour
Outgassed - No
Glass Cloth - Style 181
Cure Assembly - 445° F, 120 psi, one hour
Post-Cure - None

TABLE VI

Lap-Shear Strengths (Series 44-5)
Bis(epoxybutyl)carborane - 3 phr BF_3:$EtNH_2$

Specimen Number	Test Temperature° F	Test Atmosphere	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-5-1	75	Air	0.009	1670	adhesive
44-5-2	75	Air	0.009	820 (1)	cohesive
44-5-3	75	Air	0.006	1750	adhesive *
44-5-4	400	Air	0.006	320	adhesive *
44-5-5	400	Air	0.009	150	adhesive
44-5-6	400	Air	0.006	440	adhesive *
44-5-7	400	N_2	0.009	390	adhesive *
44-5-8	400	N_2	0.007	465	adhesive *
44-5-9	400	N_2	0.007	820	adhesive *
44-5-10	400	N_2	0.007	310	adhesive *

(1) attributed to poor surface preparation
* slightly cohesive

Composition - 2.04g epoxy + 0.06g catalyst
B-stage - 212° F for one hour
Outgassed - No
Glass Cloth - Style 181
Cure Assembly - 445° F, 120 psi, one hour
Post-Cure - None

TABLE VII

Lap-Shear Strength (Series 44-6)
Bis(epoxybutyl)carborane - 3 phr BF_3:$EtNH_2$

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-6-1	75	0.006	1700	adhesive
44-6-2	75	0.005	1700	adhesive
44-6-3	75	0.006	1975	adhesive
44-6-4	350	0.005	1940	adhesive *
44-6-5	no test - poor temperature control			
44-6-6	350	0.006	2200	adhesive *
44-6-7	350	0.007	1800	adhesive *
44-6-8	375	0.007	506	adhesive
44-6-9	375	0.006	500	adhesive *
44-6-10	375	0.007	1120	cohesive

* slightly cohesive

Composition - 2.02g epoxy + 0.06g catalyst
B-stage - 212° F for one hour
Outgassed - no
Glass Cloth - Style 181
Cure Assembly - 445° F, 120 psi, one hour
Post-Cure - None

TABLE VIII

Lap-Shear Strength (Series 44-8)
Bis(epoxybutyl)carborane - 3 phr BF_3:$EtNH_2$

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-8-1	75	0.002	1720	adhesive
44-8-2	75	0.002	1790	adhesive
44-8-3	75	0.005	1900	adhesive
44-8-4	400	0.003	720	adhesive
44-8-5	not tested - voids in overlap area			
44-8-6	400	0.007	980	adhesive
44-8-7	400	0.007	950	adhesive
44-8-8	500	0.005	140	adhesive
44-8-9	500	0.006	200	adhesive
44-8-10	500	0.007	290	adhesive

Composition - 2.01g epoxy + 0.06g catalyst
B-stage - 212° F for one hour
Outgassed - yes
Glass Cloth - None
Cure Assembly - 445° F, 120 psi, one hour
Post-Cure - None

TABLE IX

Lap-Shear Strengths (Series 44-10)
Bis(epoxybutyl)carborane - 3 phr BF_3:$EtNH_2$
Aluminum Filler (45 phr) - Stock Grade *

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength ** psi
44-10-1	75	0.006	1340
44-10-2	75	0.007	1470
44-10-3	400	0.006	280
44-10-4	400	0.007	310
44-10-5	400	0.006	340

* mixed in after B-stage
** all failures were cohesive

Composition - 1.98g epoxy, 0.06g catalyst, 0.90g aluminum *
B-stage - 212° F for one hour
Outgassed - yes
Glass Cloth - Style 181
Cure-Assembly - 445° F, 120 psi, one hour
Post-Cure - none

TABLE X

Lap-Shear Strengths (Series 44-11)
Bis(epoxybutyl)carborane - 3 phr BF_3:$EtNH_2$
Aluminum Filler (13 phr) - Stock Grade *

Specimen Number	Test Temperature	Glue Line Thickness (in)	Failure Strength *** psi
44-11-1	75	0.005	1720
44-11-2	75	0.004	1765
44-11-3	75	0.005	1720
44-11-4	75	0.006	1620
44-11-5	400	0.006	845
44-11-6	400	0.005	620
44-11-7	400	0.005	525
44-11-8 **	400	0.005	640
44-11-9 **	400	0.005	560
44-11-10 **	400	0.006	350

* mixed in after B-stage
** post-cure at 445° F for one hour
*** all failures were cohesive

Composition - 2.03g epoxy, 0.06g catalyst, 0.26g aluminum *
B-stage - 212° F for one hour
Outgassed - yes
Glass Cloth - Style 181
Cure-Assembly - 445° F, 120 psi, one hour
Post-Cure - as indicated

TABLE XI

Lap-Shear Strengths (Series 44-12)
Bis(epoxybutyl)carborane - 3 phr BF_3:$EtNH_2$
Aluminum Filler (27 phr) - 1-131 Reynolds Grade*

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength** psi
44-12-1	75	0.008	2060
44-12-2	75	0.008	1980
44-12-3	75	0.007	1980
44-12-4	75	0.008	1670
44-12-5	300	0.007	1590
44-12-6	300	0.008	1360
44-12-7	400	0.007	480
44-12-8	400	0.007	490
44-12-9	400	0.007	440
44-12-10	not tested		

* mixed in after B-stage
** all failures were cohesive

Composition - 2.02g epoxy, 0.05g catalyst, 0.54g aluminum *
B-stage - 212° F for one hour
Outgassed - yes
Glass Cloth - Style 181
Cure-Assembly - 445° F, 50 psi, one hour
Post-Cure - none

TABLE XII

Lap-Shear Strengths (Series 44-13)
Bis(epoxybutyl)carborane - 29 phr G-50 Hardener

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi *
44-13-1	75	0.005	2200
44-13-2	75	0.004	2000
44-13-3	400	0.003	1280
44-13-4	400	0.002	880
44-13-5	450	0.003	560
44-13-6	450	0.004	430
44-13-7	450	0.003	480
44-13-8	500	0.003	470
44-13-9	500	0.003	220
44-13-10	500	0.004	250

* all failures were cohesive

Composition - 2.03g epoxy + 0.58g hardener
B-stage - 212-275° F for 30 minutes plus one hour at 300° F
Outgassed - yes
Glass Cloth - Style 181
Cure-Assembly - 445° F, 120 psi, 2 hours
Post-Cure - none

TABLE XIII

Lap-Shear Strength (Series 44-14)
Bis(epoxybutyl)carborane - 30 phr G-50 Hardener

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-14-1	75	0.009	1270	adhesive
44-14-2	75	0.008	1200	adhesive
44-14-3	75	0.008	1060	adhesive
44-14-4	75	0.003	1180	adhesive
44-14-5	75	0.007	1140	adhesive
44-14-6	75	0.005	1840	adh-coh
44-14-7	75	0.006	1770	adh-coh
44-14-8	400	0.004	1880	cohesive
44-14-9	400	0.006	1720	cohesive
44-14-10	400	0.006	1325	adh-coh

Composition - 2.02g epoxy + 0.60g hardener
B-stage - 266-302° F for 60 minutes followed by 300° F for 75 minutes *
Outgassed - yes
Glass Cloth - Style 181
Cure Assembly - 445° F, 120 psi, 2 hours
Post-Cure - None

* The overlap surfaces were primed in this work. Two B-staged samples were prepared as described above. One sample was dissolved in 3 ml of methylene chloride and the solution was applied with a medicine dropper to the overlap area of the specimens. The samples were air dried for 15 minutes at room temperature and in vacuo for 15 minutes at 100° C. The second B-staged epoxy sample was applied to the overlap area in the usual manner. Glass cloth carrier was soaked in the residual methylene chloride - B-staged epoxy sample, air dried and placed in the overlap area. The specimens were outgassed and cured as described above.

TABLE XIV

Lap-Shear Strengths (Series 44N-16)
Bis(epoxybutyl)-neo-carborane - 28 phr G-50 Hardener

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44N-16-1	75	0.004	2000	cohesive
44N-16-2	75	0.004	1830	cohesive
44N-16-3 *	75	0.003	1340	cohesive
44N-16-4 *	75	0.003	1520	cohesive
44N-16-5	400	0.004	440	coh-ad
44N-16-6	400	0.003	580	coh-ad
44N-16-7	400	0.005	610	cohesive
44N-16-8 *	400	0.005	920	cohesive
44N-16-9	500	0.004	150	cohesive
44N-16-10	500	0.004	225	cohesive
44N-16-11 **	75	0.003	1500	cohesive
44N-16-12 **	75	0.005	1000	cohesive
44N-16-13 **	400	0.004	510	cohesive
44N-16-14 **	500	0.004	200	coh-ad
44N-16-15 **	500	0.004	180	coh-ad

* post cure at 550° F for two hours
** additional B-stage

Composition - 2.02g epoxy + 0.56g hardener
B-stage - 300° F for 2-1/4 hours. Specimens 1-10
Specimens 11-15 received an additional 3 hours post-cure at 300° F
Outgassed - yes
Glass cloth - Style 181
Cure-Assembly - 445° F, 120 psi, 2 hours
Post-Cure - as indicated

TABLE XV

Lap-Shear Strengths (Series 44N-17)
Bis(epoxybutyl)-neo-carborane - 30 phr G-50 Hardener

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44N-17-1*	75	0.004	1230	adhesive
44N-17-2*	75	0.004	1040	adhesive
44N-17-3*	400	0.005	365	adhesive
44N-17-4 **	400	0.005	1090	cohesive
44N-17-5 **	400	0.004	1020	cohesive
44N-17-6 **	500	0.005	260	cohesive
44N-17-7*	500	0.005	110	cohesive

* cured at 445° F
** cured at 420° F

Composition - 2.0g epoxy + 0.63g hardener
B-stage - 300° F, 5-3/4 hours
Outgassed - yes
Glass Cloth - Style 181
Cure-Assembly - as indicated at 120 psi, 2 hours
Post-Cure - none

TABLE XVI

Lap-Shear Strengths (Series 44-19)
Bis(epoxybutyl)carborane - 47 phr G-50 Hardener

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-19-1	75	0.005	2040	cohesive
44-19-2	75	0.005	1850	coh-ad
44-19-3	75	0.007	1420	coh-ad
44-19-4	75	0.006	1950	cohesive
44-19-5	500	0.006	660	cohesive
44-19-6	500	0.004	520	cohesive
44-19-7	500	0.006	830	coh-ad
44-19-8	500 *	0.006	1730	coh-ad **
44-19-9	500 *	0.005	970	cohesive **
44-19-10	500 *	0.006	890	cohesive **

* post-cured at 500° F - two hours
** epoxy dark brown outside overlap area, slightly yellow inside

Composition - 1.51g epoxy + 0.71g hardener
B-stage - 300° F for 40 minutes
Outgassed - yes
Glass Cloth - Style 112
Cure-Assembly - 390° F, 120 psi, 2-1/2 hours
Post-Cure - as indicated

TABLE XVII

Lap-Shear Strengths (Series 44-20)
Bis(epoxybutyl)carborane - 48 phr G-50 Hardener

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-20-1	75	0.006	1070	coh-ad
44-20-2	75	0.006	1200	cohesive
44-20-3	75	0.004	1150	coh-ad
44-20-4	75	0.004	1450	cohesive
44-20-5	500	0.006	1270	cohesive
44-20-6	500	0.005	1580	cohesive
44-20-7	500	0.005	1340	cohesive
44-20-8	500	0.005	1060	cohesive
44-20-9	500 *	0.004	1300	cohesive **
44-20-10	500 *	0.004	1460	cohesive **

* post-cured an additional 22 hours at 500° F

** epoxy almost black outside overlap area and yellow-brown inside

Composition - 1.51g epoxy + 0.73g hardener
B-stage - 300° F for 45 minutes
Outgassed - yes
Glass Cloth - Style 112
Cure-Assembly - 390° F, 120 psi, 2 hours
Post-Cure - two hours at 500° F plus as indicated

TABLE XVIII

Lap-Shear Strengths (Series 44-21)
Bis(epoxybutyl)carborane - 47 phr G-50 Hardener

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-21-1	75	0.004	1900	cohesive
44-21-2	75	0.005	2000	cohesive
44-21-3 *	75	0.005	1230	cohesive
44-21-4 *	75	0.005	1690	cohesive
44-21-5 *	75	0.005	1120	coh-ad
44-21-6 *	75	0.004	1390	cohesive
44-21-7 *	500	0.004	1540	cohesive
44-21-8 *	500	0.005	750	cohesive
44-21-9 *	500	0.005	700	cohesive
44-21-10 *	500	0.004	1170	cohesive

* post-cured 500° F for two hours

Composition - 1.48g epoxy + 0.70g hardener
B-stage - 300° F for 40 minutes
Outgassed - yes
Glass Cloth - Style 112
Cure-Assembly - 390° F, 120 psi, 2 hours
Post-Cure - as indicated

TABLE XIX

Lap-Shear Strengths (Series 44-22)
Bis(epoxybutyl)carborane - 47 phr G-50 Hardener

Specimen Number	Test Temperature ° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-22-1	75	0.004	1800	coh-ad
44-22-2	75	0.004	1550	coh-ad
44-22-3 *	75	0.003	1470	adhesive
44-22-4 *	75	0.004	1460	coh-ad
44-22-5 *	500	0.003	910	adhesive
44-22-6 *	500	0.004	810	adhesive
44-22-7 **	75	0.004	1400	coh-ad
44-22-8 **	75	0.003	560	coh-ad
44-22-9 **	500	0.004	340	coh-ad
44-22-10 **	500	0.004	220	coh-ad

* post-cured at 500° F for 4 hours
** post-cured at 400° F for 24 hours

Composition - 1.48g epoxy + 0.72g hardener
B-stage - 300° F for 35 minutes
Outgassed - yes
Glass Cloth - Style 112
Cure-Assembly - 390° F, 60 psi, 2-1/2 hours
Post-Cure - as indicated

TABLE XX

Lap-Shear Strengths (Series 44-23)
Bis(epoxybutyl)carborane - 50 phr G-50 Hardener

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
44-23-1	75	0.003	1680	adhesive
44-23-2	75	0.004	1840	adhesive
44-23-3	500	0.004	240	coh-ad
44-23-4	500	0.004	220	coh-ad
44-23-5 *	75	0.004	1510	adhesive
44-23-6 *	75	0.004	1370	adhesive
44-23-7 *	500	0.004	775	adhesive
44-23-8 *	500	0.004	730	adhesive
44-23-9 **	75	0.003	480	coh-ad
44-23-10 **	75	0.003	300	coh-ad

* post-cured at 400° F for 4 hours
** post-cured at 400° F for 24 hours

Composition - 1.51g epoxy + 0.75g hardener
B-stage - 300° F for 45 minutes
Outgassed - yes
Glass Cloth - Style 112
Cure-Assembly - 356° F, 60 psi, 2-1/2 hours
Post-Cure - as indicated

TABLE XXI

Lap-Shear Strengths (Series 55-1)
Bis(epoxypentyl)carborane - 3 phr BF_3:$EtNH_2$

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
55-1-1	75	0.006	2810	cohesive
55-1-2	75	0.005	2740	cohesive

Composition - 1.0g epoxy + 0.030g catalyst
B-stage - 225-260° F for 30 minutes
Outgassed - no
Glass Cloth - Style 181
Cure-Assembly - 445° F, 120 psi, 1 hour
Post-Cure - none

TABLE XXII

Lap-Shear Strength (Series 55-2)
Bis(epoxypentyl)carborane - 3 phr BF_3:$EtNH_2$

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
55-2-1	75	0.006	2324	coh-ad
55-2-2	75	0.005	2886	cohesive
55-2-3	500	0.005	130	adhesive
55-2-4	500	0.004	240	adhesive

Composition - 2.04g epoxy and 0.06g catalyst
B-stage - 212° F for 50 minutes
Outgassed - no
Glass Cloth - Style 181
Cure-Assembly - 445° F, 120 psi, 1 hour
Post-Cure - none

TABLE XXIII

Lap-Shear Strengths (Series 66-1)
Bis(epoxyhexyl)carborane - 3 phr BF_3:$EtNH_2$

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
66-1-1	75	0.007	3280	cohesive
66-1-2	75	0.007	3600	cohesive
66-1-3	75	0.006	3400	cohesive

Composition - 1.02g epoxy + 0.03g catalyst
B-stage - 230-265° F for 30 minutes
Outgassed - no
Glass Cloth - Style 181
Cure-Assembly - 445° F, 120 psi, one hour
Post-Cure - none

TABLE XXIV

Lap-Shear Strengths (Series 66-4)
Bis(epoxyhexyl)carborane - 1 phr DMP-30

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
66-4-1 to 5	75	not tested *	-	-
66-4-6	75	0.004	1360	cohesive
66-4-7	75	not tested **	-	-
66-4-8	75	0.005	1730	cohesive
66-4-9	75	0.002	1600	cohesive
66-4-10	75	0.002	1150	cohesive

* incomplete cure
** defective specimen

Composition - 2.02g epoxy and 0.02g catalyst
B-stage - 212° F for one hour
Outgassed - yes
Glass Cloth - Style 181
Cure-Assembly - 425° F, 120 psi, one hour (Specimens 1-5)
575° F, 120 psi, one hour (Specimens 6-10)

TABLE XXV

Lap-Shear Strengths (Series 66-3)
Bis(epoxyhexyl)carborane - 20 phr Phthalic Anhydride - 1 phr BF_3:$EtNH_2$

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
66-3-1 *	75	0.006	1710	cohesive (1)
66-3-2 *	75	0.006	1920	cohesive (1)
66-3-3 *	75	0.005	2330	cohesive (1)
66-3-4 *	75	0.006	1000	cohesive (1)
66-3-5 *	75	0.005	1240	cohesive (1)
66-3-6	75	0.005	1430	adhesive (2)
66-3-7	75	0.006	2040	adhesive (2)
66-3-8	75	0.007	1810	adhesive (2)
66-3-9	75	not tested - defective		
66-3-10	75	0.003	2280	adhesive (2)

* Specimens outgassed prior to curing - phthalic anhydride sublimes
1 Some adhesive failure
2 Partly cohesive failure

Composition - 1.01g epoxy, 0.01g BF_3:$EtNH_2$, 0.20g phthalic anhydride
B-stage - 212° F for 4 minutes
Outgassed - Specimens 1-5 only
Glass Cloth - Style 181
Cure-Assembly - 400° F, 120 psi, one hour
Post-Cure - none

TABLE XVI

Lap-Shear Strengths (Series 66-7)
Bis(epoxyhexyl)carborane - 20 phr Phthalic Anhydride - 2 phr DMP-30

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
66-7-1	75	0.004	2480	cohesive
66-7-2	75	0.004	2180	cohesive
66-7-3	75	0.004	2680	cohesive
66-7-4	75	0.004	2200	cohesive
66-7-5	75	0.003	2140	cohesive
66-7-6 *	75	0.003	3210	cohesive
66-7-7 *	75	0.002	3100	cohesive
66-7-8 *	75	0.003	3220	cohesive
66-7-9 *	75	0.004	2930	cohesive
66-7-10 *	75	0.004	3000	cohesive

* cured for 2 hours

Composition - 2.12g epoxy, 0.39g phthalic anhydride, 0.05g DMP-30
B-stage - 150° F for 20 minutes
Outgassed - no
Glass Cloth - none
Cure Assembly - 445° F, 120 psi, one hour - Specimens 1-5
445° F, 120 psi, two hours - Specimens 6-10

TABLE XXVII

Lap-Shear Strengths (Series 66-8)
Bis(epoxyhexyl)carborane - 20 phr Phthalic Anhydride - 3 phr DMP-30

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi *
66-8-1	75	0.005	2020
66-8-2	75	0.005	1920
66-8-3	75	0.005	2140
66-8-4	75	0.007	2240
66-8-5	75	0.002	2640
66-8-6	not tested		
66-8-7	75	0.005	2400
66-8-8	75	0.006	2120
66-8-9	400	0.004	100
66-8-10	400	0.004	170

* all failures were cohesive

Composition - 2.03g epoxy, 0.40g phthalic anhydride, 0.07g DMP-30
B-stage - 150° F for 35 minutes
Outgassed - No
Glass Cloth - Style 181
Cure-Assembly - 445° F, 120 psi, 3 hours - Specimens 1-5
445° F, 120 psi, 2 hours - Specimens 6-10

TABLE XXVIII

Lap-Shear Strengths (Series 66-9)
Bis(epoxyhexyl)carborane - 20 phr Phthalic Anhydride - 3 phr DMP-30

Specimen Number	Cure Conditions	Post-cure Conditions	Glue Line Thickness (in)	Failure Strength psi
66-9-1	300° F - 120 psi-one hour	-	0.004	560
66-9-2	"	-	0.003	440
66-9-3	"	480° F - one hour	0.003	1060
66-9-4	"	"	0.005	1260
66-9-5	"	"	0.007	1300
66-9-6	300° F - 120 psi-two hours	one hour 480° F one hour 445° F	0.005	2460
66-9-7	"	"	0.005	2510
66-9-8	"	"	0.005	1900
66-9-9	"	"	0.006	2380
66-9-10	"	"	0.005	2380

Composition - 2.02g epoxy, 0.37g phthalic anhydride, 0.04g DMP-30
B-stage - 175° F for 30 minutes
Outgassed - No
Glass Cloth - Style 181
Cure-Assembly - as indicated
Post-Cure - as indicated

TABLE XXIX

Lap-Shear Strengths (Series 66-10)
Bis(epoxyhexyl)carborane - 3 phr BF_3:$EtNH_2$

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
66-10-1	75	0.003	2950	cohesive
66-10-2	75	0.002	2500	cohesive
66-10-3	75	0.003	2000	adhesive
66-10-4	250	0.002	1270	adhesive
66-10-5	250	0.005	1980	adhesive
66-10-6	275	0.004	460	adhesive
66-10-7	275	0.004	290	adhesive
66-10-8	300	0.003	330	adhesive
66-10-9	300	0.003	240	adhesive

Composition - 2.03g epoxy and 0.06g catalyst
B-stage - 212° F for 90 minutes
Outgassed - yes
Glass Cloth - Style 181
Cure-Assembly - 445° F, 120 psi, one hour
Post-Cure - None

TABLE XXX

Lap-Shear Strengths (Series 66-11)
Bis(epoxyhexyl)carborane - 3 phr BF_3:$EtNH_2$

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
66-11-1	75	0.010	2480	coh-ad
66-11-2	75	0.010	2450	cohesive
66-11-3	75	0.012	1160	coh-ad
66-11-4	225	0.010	420	coh-ad
66-11-5	225	0.011	620	coh-ad
66-11-6	225	0.010	880	coh-ad
66-11-7	225	0.013	480	cohesive
66-11-8	225	0.012	240	coh-ad
66-11-9	225	0.012	340	coh-ad
66-11-10	225	0.013	245	coh-ad

Composition - 2.14g epoxy and 0.06g catalyst
B-stage - 255° F for 75 minutes
Outgassed - yes
Glass Cloth - Style 181
Cure-Assembly - 445° F, 120 psi, one hour
Post-Cure - None

TABLE XXXI

Lap-Shear Strengths (Series 66-12)
Bis(epoxyhexyl)carborane - 39 phr G-50 Hardener

Specimen Number	Test Temperature° F	Glue Line Thickness (in)	Failure Strength psi	Type of Failure
66-12-1	75	0.003	2860	cohesive
66-12-2	75	0.003	3200	cohesive
66-12-3	500	0.003	235	cohesive
66-12-4	500	0.003	200	cohesive
66-12-5 (1)	500	0.003	120	cohesive
66-12-6 *	75	0.004	2480	cohesive
66-12-7 *	75	0.003	2740	cohesive
66-12-8 * (1)	75	0.003	1660	cohesive
66-12-9 * (1)	75	0.004	1240	cohesive
66-12-10 * (1)	500	0.004	110	cohesive

* additional B-stage (one hour at 350° F)
(1) post-cured 500° F for two hours

Composition - 1.50g epoxy + 0.59 hardener
B-stage - 300-356° F for 3 hours (also as indicated)
Outgassed - yes
Glass Cloth - Style 112
Cure Assembly - 390° F, 60 psi, 2-1/2 hours
Post-Cure - as indicated