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Formulation and Characterization of Epoxy Resin Copolymer for Graphite Composites

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CONTRACT NAS2-10130

NASA

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Formulation and Characterization of Epoxy Resin Copolymer for Graphite Composites

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Prepared for
Ames Research Center
under Contract NAS2-10130

National Aeronautics and
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This report summarises work conducted by the Advanced Manufacturing Technology organisation, Missile Systems Division (MSD), of Lockheed Missiles & Space Company, Inc., Sunnyvale, California, 94086, under NAS 2-10130 Contract. Previous work had been done by Fred L. Keck of the Manufacturing Research organisation which was partially absorbed into Advanced Manufacturing Technology. The administration of the work is under the direction of NAS/Ames Research Center with D. A. Kourtides the Technical Monitor. Technical assistance and synthesis of diglycidyl ether of bis (4-hydroxyphenyl) fluorene (DGEBF) was provided by Dr. H. A. Newey and C. J. Busso of Newey & Busso Associates.

SUMMARY

Maximum char yield was obtained with a copolymer containing 25% mol fraction DGEBF and 75% mol fraction DGEBA (Epon 828). To achieve the high values (above 40%), a large quantity of catalyst (trimethoxyboroxine) was necessary. Although a graphite laminate 1/8" thick was successfully fabricated, the limited life of the catalyzed epoxy copolymer system precludes commercial application.

Char yields of 45% can be achieved with phenolic cured epoxy systems as indicated by data generated under NAS 2-10207 contract. A graphite laminate using this type of resin system was fabricated for comparison purposes. The resultant laminate was easier to process and because the graphite prepreg is more stable, the fabrication process could readily be adapted to commercial applications.

INTRODUCTION

One of the problems associated with graphite composites is the containment of the carbon fibers when the composite burns. Free carbon fibers can provide conductive paths leading to serious electrical problems. To minimize this possibility, the resin matrix selected for a composite should have the property of producing a large quantity of intact char when burned. In addition, the resin matrix should have good handling properties, good mechanical properties when cured, good moisture resistance, and a glass transition temperature high enough for the intended application.

From the literature(1) copolymers of diglycidyl ether of bis (4-hydroxyphenyl) fluorene (DGEBF) and the diglycidyl ether of bisphenol A (DGEBA) cured with trimethoxyboroxine (TMB) possess these desirable characteristics with regard to char formation and containment of graphite fibers during a fire. The objective of this contract is the synthesis of sufficient DGEBF for char formation optimization of this epoxy resin blend and subsequent evaluation as a laminating resin in a graphite composite.

Since the nature of NAS2-10207 contract is similar, i.e. evaluation of commercially available epoxy resins cured with phenolic resins for char resistance, pertinent data will be included for comparison purposes. In addition, to make the results more meaningful, a laminate will be prepared using the best epoxy/phenolic system evaluated plus a laminate incorporating concepts of both contracts.

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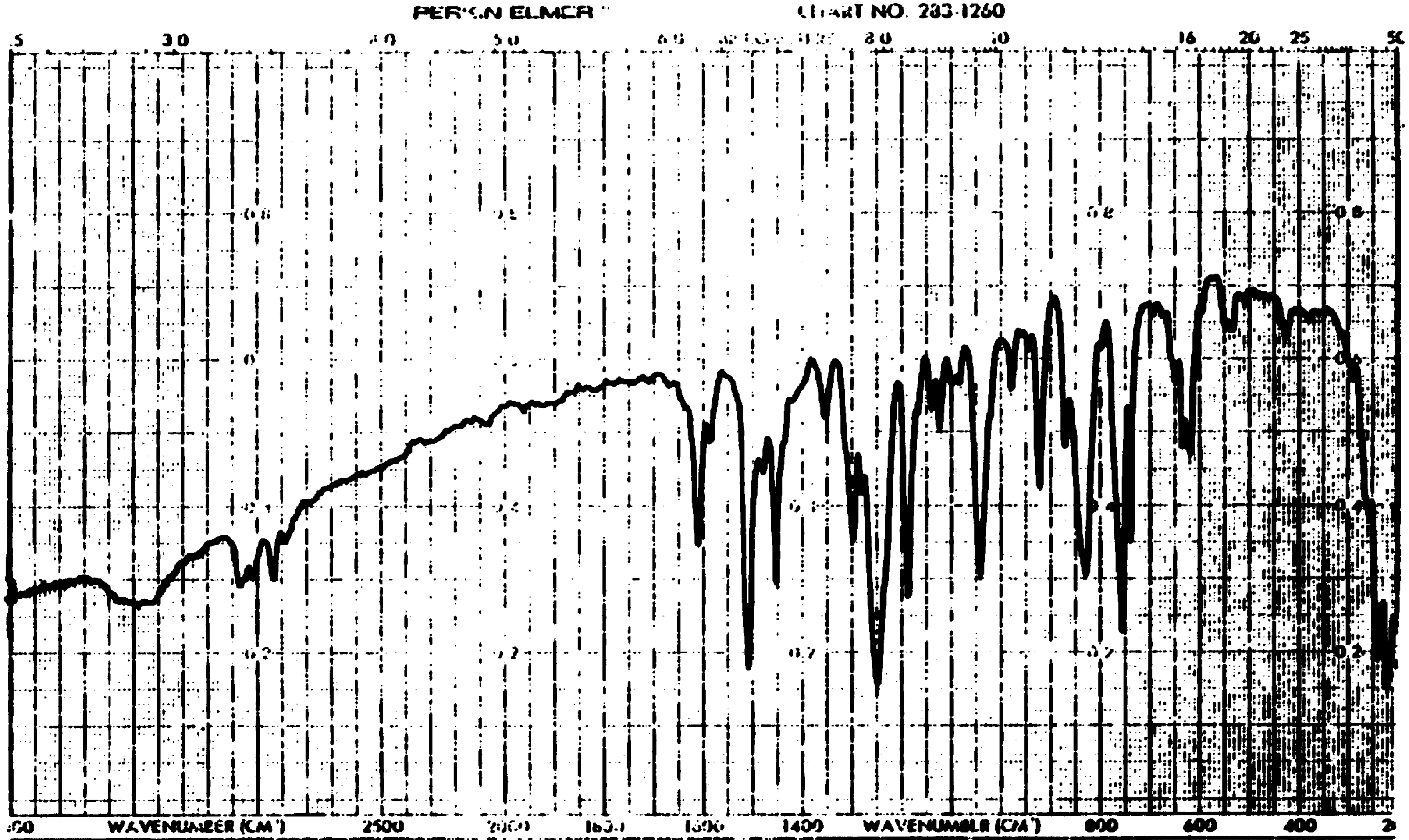
(1) Kourtides, D. A. and Parker, J. A., Science of Advanced Materials and Process Engineering Series, 23, 893-912 (Anaheim, May 1978).

RESIN SYNTHESIS & MONOMER CHARACTERIZATION

Eighteen hundred and fifty grams of crystalline DGEBF were synthesized having an epoxy value of 0.40 equivalents per 100 grams of resin and a hydrolyzable chlorine content of 0.016% by weight. The synthesis was conducted with the assistance of Dr. H. A. Newey and C. J. Busso of Newey & Busso Associates. Similar material from Dr. Eli M. Pearce, Head, Chemistry Dept., of Polytechnic Institute of New York was analyzed and found to contain 0.38 equivalents per 100 grams and 0.53% by weight hydrolyzable chlorine. The 1850 grams represents the combined product of five separate preparations which were subjected to various treatments to lower the hydrolyzable chlorine content. An infrared spectrum of this material is shown in Figure 1. Data summarizing the various preparations can be found in Table 1.

Preparation	Description	Epoxy Equivalent	Hydrolyzable Chlorine
1	Non-crystalline resin	0.37	1.08
2	Non-crystalline resin	0.36	0.80
3	Non-crystalline resin	0.39	1.83
4A	Crystallized fraction } 2-1/2 mol	0.39	0.79
4B	Non-crystallized fraction } scale-up	0.34	1.38
	Retreated Run #1, #2, #3 and 4B. (non-crystalline)	0.393	0.054
	Retreated 4A (crystalline)	0.39	0.40
5	Crystalline product (2-1/2 mol scale-up)	0.41	0.28
	Crystalline product of Runs 4 & 5 remaining after filtration	0.408	0.021
	Crystalline product of Runs 4 & 5 recovered from filtrate.	0.392	0.035
	Recrystallized blend of all preparations	0.40	0.016
	Polytechnic Sample (E. Pearce)	0.38	0.53

TABLE 1



ABSCISSA
EXPANSION
SUPPRESSION

ORDINATE
EXPANSION 1X
% T ✓ ABS

SCAN TIME 12 min
RESPONSE
SLIT PROGRAM

REP. SCAN SINGLE BEAM
TIME DRIVE PRE SAMPLE CHOP
OPERATOR RCT DATE 5-28-[illegible]

SAMPLE DGEBF
ORIGIN

REMARKS
Cast from chloroform sol'n
Soluble in methylene chloride too

SOLVENT
CONCENTRATION

CELL PATH Film | KBr
REFERENCE

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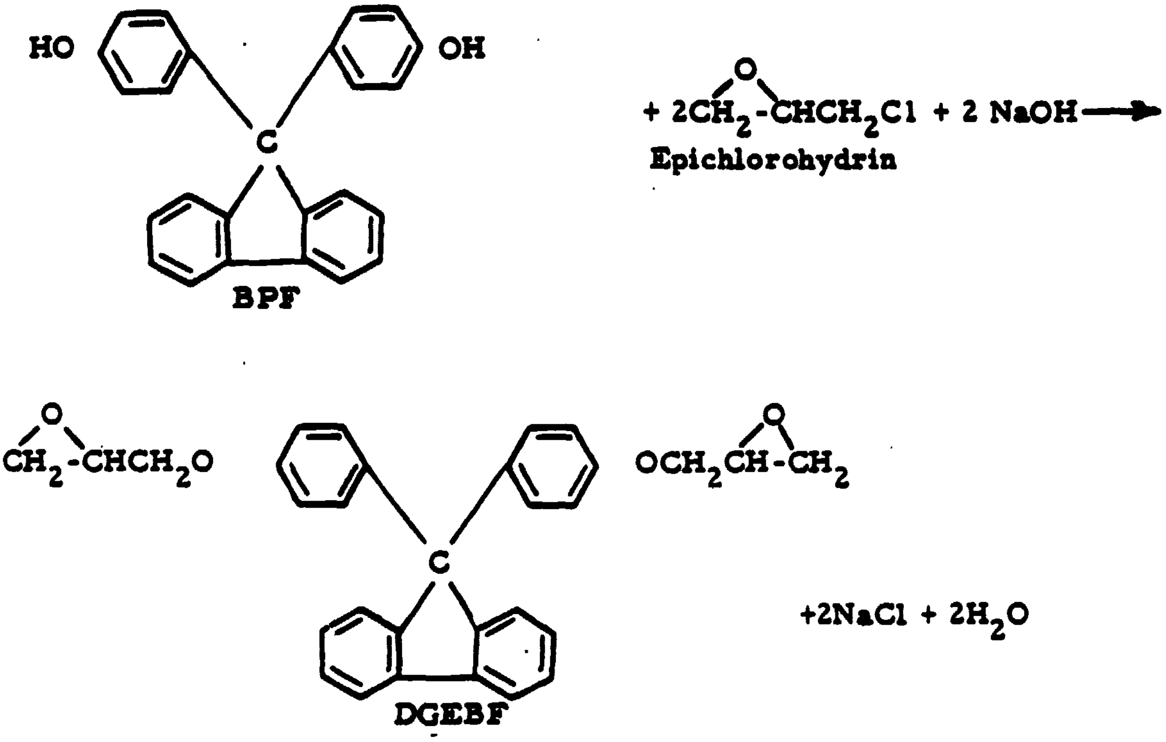
FIGURE 1

Preparation of DGEBF can be represented in an ideal case by the following equation:



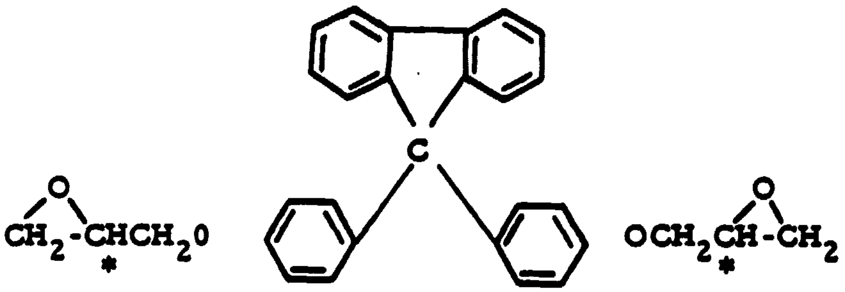
In practice the reaction is carried out using a five fold excess of epichlorohydrin to suppress reactions that lead to higher molecular weight products.

A detailed description of the finalized process can be found in the appendix. Figure 2 depicts the equipment for a 5 liter flask (2-1/2 mol) preparation. To lower the hydrolyzable chlorine content which interferes with resin cure using Lewis acids, the products of several preparations were combined, reconstituted in methylisobutyl ketone (MIBK) and retreated with additional caustic. The following reversible equation applies:

$$\text{R-O-CH}_2\text{-}\overset{\text{OH}}{\text{CH}}\text{-CH}_2\text{Cl} + \text{NaOH} \rightleftharpoons \text{R-O-CH}_2\text{-}\overset{\text{O}}{\overbrace{\text{CH-CH}_2}} + \text{NaCl} + \text{H}_2\text{O}$$

Removal of the NaCl followed by neutralisation of the remaining caustic with sodium phosphate (mono basic) minimises the remaining chlorohydrin groups. The bulk of the MIBK was removed by distillation followed by product crystallisation on cooling. The crystalline DGEBF was filtered and vacuum dried.

It should be noted that the crystalline nature of DGEBF probably consists of two steroisomers which have different melting points because it is a symmetrical compound containing two asymmetric carbon atoms.



*asymmetric carbon

An observation was made that the first material to crystallize melted between 145-153°C while the bulk of the product melted between 130-148°C. Apparently this material is similar to tartaric acid which has two steroisomers that melt at different temperatures.

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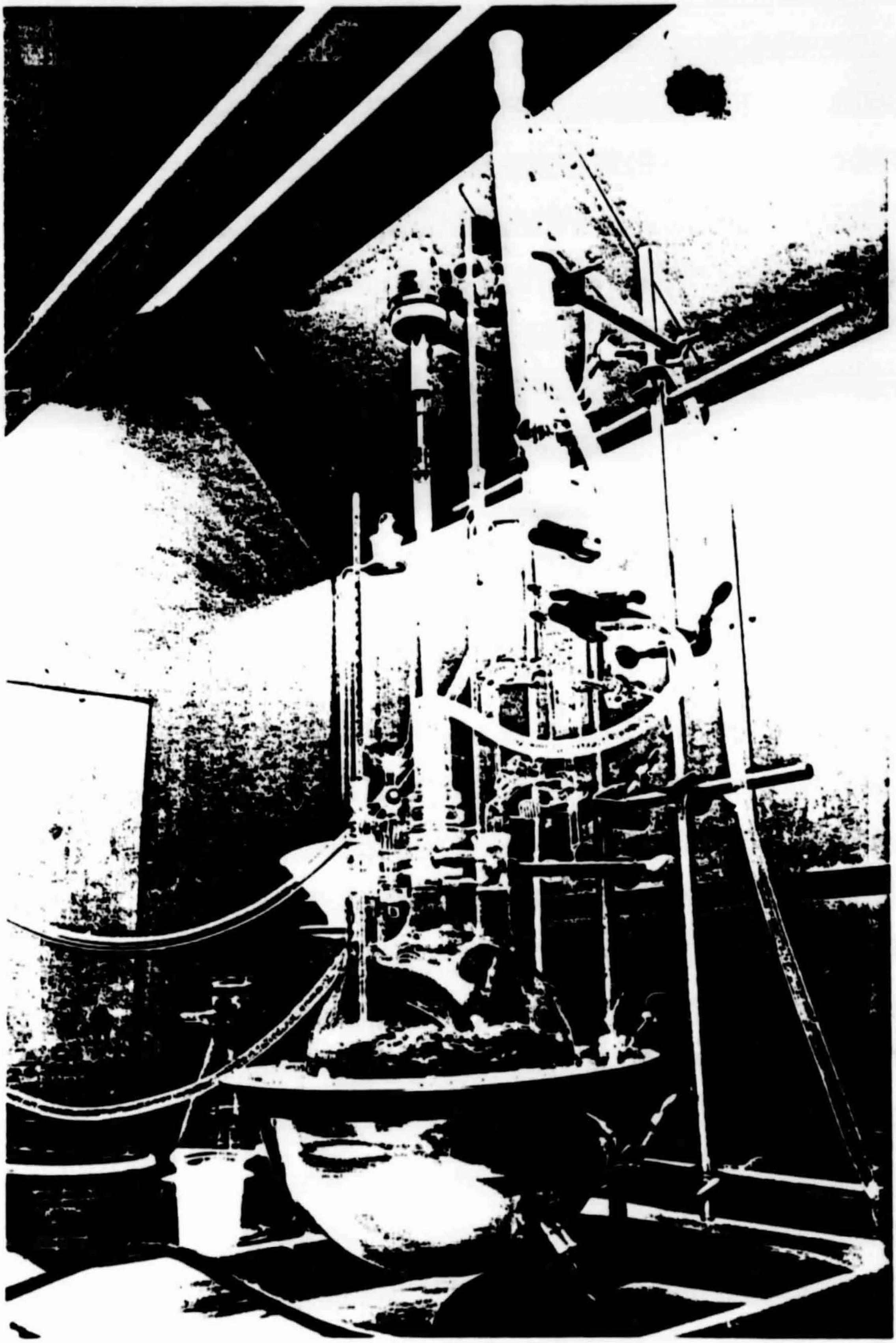


FIGURE 2

COPOLYMER EVALUATION & OPTIMIZATION

The DGEBA/DGEBF copolymer was evaluated to obtain the maximum char yield and still be suitable for graphite prepregging operations. In addition to be cost effective, the optimum formulation should contain the minimum amount of DGEBF necessary to achieve the high char value.

Preliminary evaluation of the DGEBA/DGEBF copolymer for char resistance using a DuPont 990 thermal analyzer produced thermogravimetric analysis (TGA) values significantly lower than those reported by NASA. Sample preparation using a mortar and pestle as suggested by NASA still produced comparable low char values. Using ground material or a chunk of same produced some variation, but not sufficient to account for the discrepancy. Since NASA reported significantly higher char values than LMSC on identical material, the difference had to be in the testing procedure. Further discussions with NASA indicated that the TGA differences could be caused by the quality of the nitrogen purge. Regular nitrogen (99.95% minimum purity) had been used at LMSC for the purge since purity had not specified. Changing to 99.999% minimum purity nitrogen and adjusting the flow produced TGA values similar to those reported by NASA. The effect of nitrogen quality and flow rate on TGA values of a NASA prepared copolymer (#1016) containing 25% mol fraction DGEBF is shown in Table 2. For comparison purposes the "low" preliminary data on a similar 25% mol fraction LMSC copolymer (7-3) is included.

	% Char		Nitrogen	
Specimen	700°C	750°C	Purity	Flow ml/min
7-3	27.1	--	99.95	16
NASA 1016	28.9	25.6	99.95	16
NASA 1016	33.8	30.7	99.999	16
NASA 1016	37.6	36.2	99.999	50
NASA 1016	35.6	34.1	99.999	100
NASA 1016	36.0	--	99.999	excessive
NASA 1016 Data	--	34.5	99.998	100

TABLE 2

The data in Table 2 show the importance of nitrogen purity and flow rate. Since maximum TGA values were obtained at a flow rate of 50 ml per minute, this rate was used for copolymer optimization instead of 100 ml per minute used by NASA. An 8-9 mg sample obtained by filing the cast resin was used each time for comparison purposes.

Preliminary evaluation of the copolymer indicated that the procedure used to mix the sample had an effect on ultimate TGA value. Consequently a 22.9% mol fraction DGEBF copolymer (formulation suggested by Brooklyn Polytechnic) was prepared using the NASA procedure, LMSC procedure and a modification of the latter. All specimens prepared per the following procedures were cured under nitrogen.

1-1/2 hours @ 135°C (275°F)
3 hours @ 177°C (350°F)
3 hours @ 218°C (425°F)

NASA Procedure

1. Grind DGEBF and DGEBA in mortar and pestle.
2. Add Trimethoxyboroxine catalyst and mix.
3. Pour into glass test tube and cure as above.

LMSC Procedure

1. Mix DGEBF in DGEBA and heat on hot plate until in solution.
2. Degass and cool to ~100-120°F.
3. Add Trimethoxyboroxine catalyst gradually with stirring.
4. Re-degass until foam breaks. Note: If necessary warm to ~ 100°F before re-degassing.
5. Pour into glass test tube and cure as above.

Modified LMSC Procedure

1. Eliminate step 4 above.

Table 3 compares TGA values with method of sample preparation. The data confirm the importance of re-degassing the copolymer after addition of the trimethoxyboroxine.

	% Char		
Specimen Prep.	700°C	750°C	Comments
NASA	30.4	28.3	No degassing
LMSC	33.8	31.6	Two degassing steps
LMSC Mod.	26.4	23.8	One degassing step

CATALYST CONCENTRATION

Preliminary evaluation of the copolymer indicated that 22.9% mol fraction DGEBF had the highest char resistance. Since all systems used 9.5 grams of trimethoxyboroxine per epoxy equivalent, an investigation was made to determine the effect of varying the catalyst concentration. A 22.9% mol fraction DGEBF was selected as the copolymer ratio for the study. Table 4 compares TGA values over a range of trimethoxyboroxine catalyst concentration. All samples were prepared using the LMSC procedure.

GmsTMB/Epoxy Equiv		% Char	
		700 °C	750°C
9.5	(control)	31.7	30.2
2.375	(1/4 control)	14.5	13.5
4.75	(1/2 control)	24.3	22.1
9.5	(control)	31.0	29.8
11.875	(1-1/4 x control)	35.0	32.9
14.25	(1-1/2 x control)	36.0	33.6
19.0	(2 x control)	41.5	39.2

TABLE 4

It is evident from the above data that catalyst concentration significantly affects char resistance and that TGA values of 40% are possible by using sufficient catalyst. However, the reaction rate increases with the amount of trimethoxyboroxine which limits processibility in graphite laminates. Since previous variations had not produced TGA value of 40%, a series of copolymers having 20-35% mol fraction DGEBF was repeated using 19 grams of trimethoxyboroxine per epoxy equivalent. All of the highly catalyzed copolymer systems turned pink within one hour after degassing indicating the reaction had started without application of heat. Table 5 compares the TGA values, all of which exceeded 40% at 700°C.

Specimen	% Char 700°C	% Char 750°C	Mol Fraction DGEBF
21A	40.9	37.4	20.0
21B	42.5	41.0	22.9
21C	44.9	42.9	25.0
21D	44.3	42.4	30.0
21E	45.4	43.0	35.0

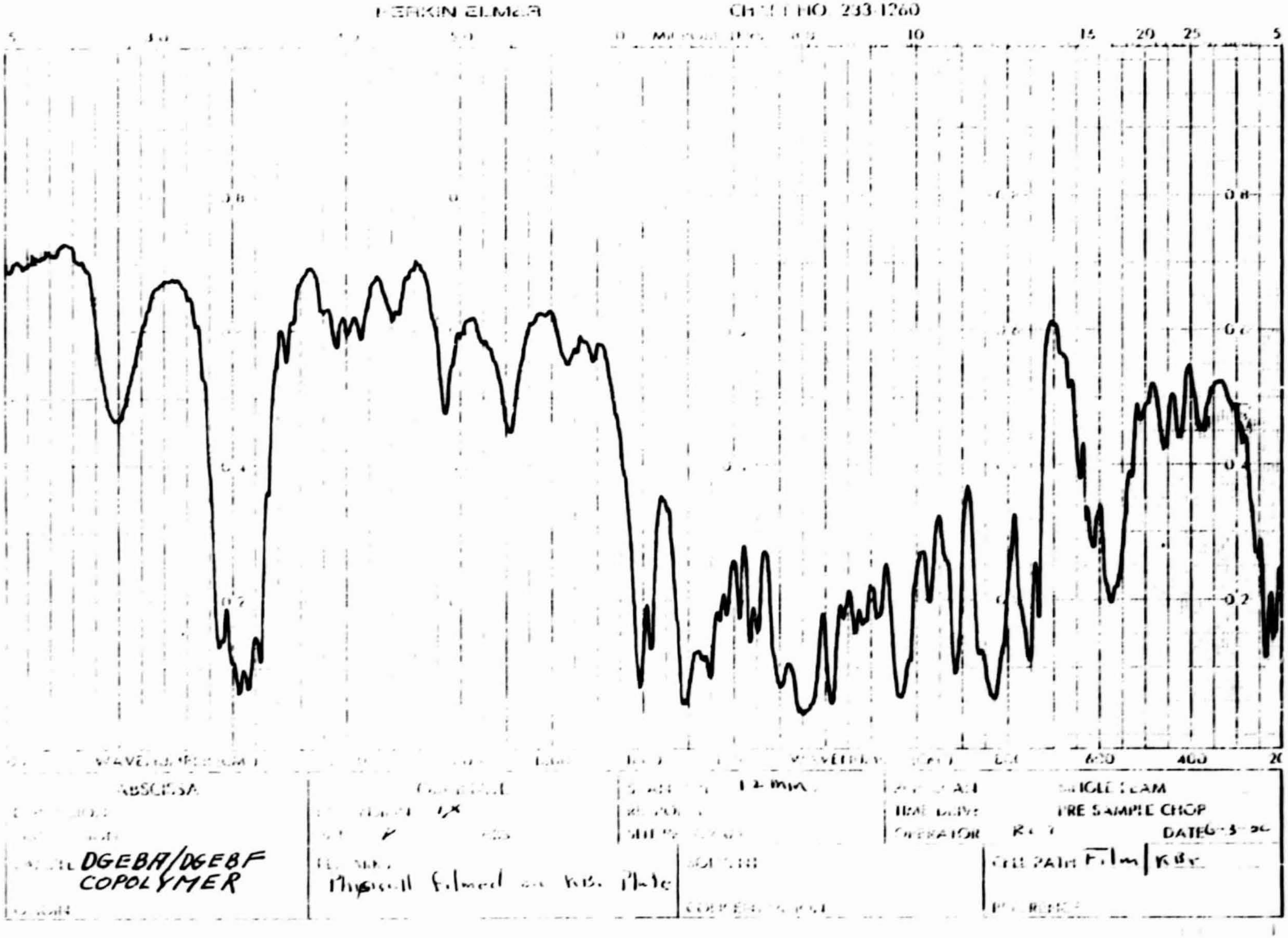
TABLE 5

From the preceeding char data the optimum copolymer blend contains 25% mol fraction DGEBF catalyzed with 19 grams of trimethoxyboroxine per epoxy equivalent. Relative quantities for this formulation are:

DGEBA (Epon 828)	10.0
DGEBF	4.1
Trimethoxyboroxine	1.35

The specific gravity of the cured system is 1.216. The uncatalyzed 25% mol fraction DGEBF copolymer is very viscous at room temperature. An infrared spectrum of this copolymer is shown in Figure 3.

When catalyzed the initiation temperature (T_i) as determined by Differential Scanning Calorimetry (DSC) is 27°C, i.e., room temperature. The scan confirms the limited life observed during evaluation of the copolymer. Similarly, the T_i for the phenolic cured DEN 438 epoxy used to make a comparison graphite laminate is 75°C. These DSC curves plus that incorporating both concepts (phenolic cured DGEBF copolymer) are shown in Figure 4.



DGEBA/DGEBF COPOLYMER

Physically filmed on KBr Plate

12 min

Film | KBr

FIGURE 3

DIFFERENTIAL SCANNING CALORIMETRY DATA

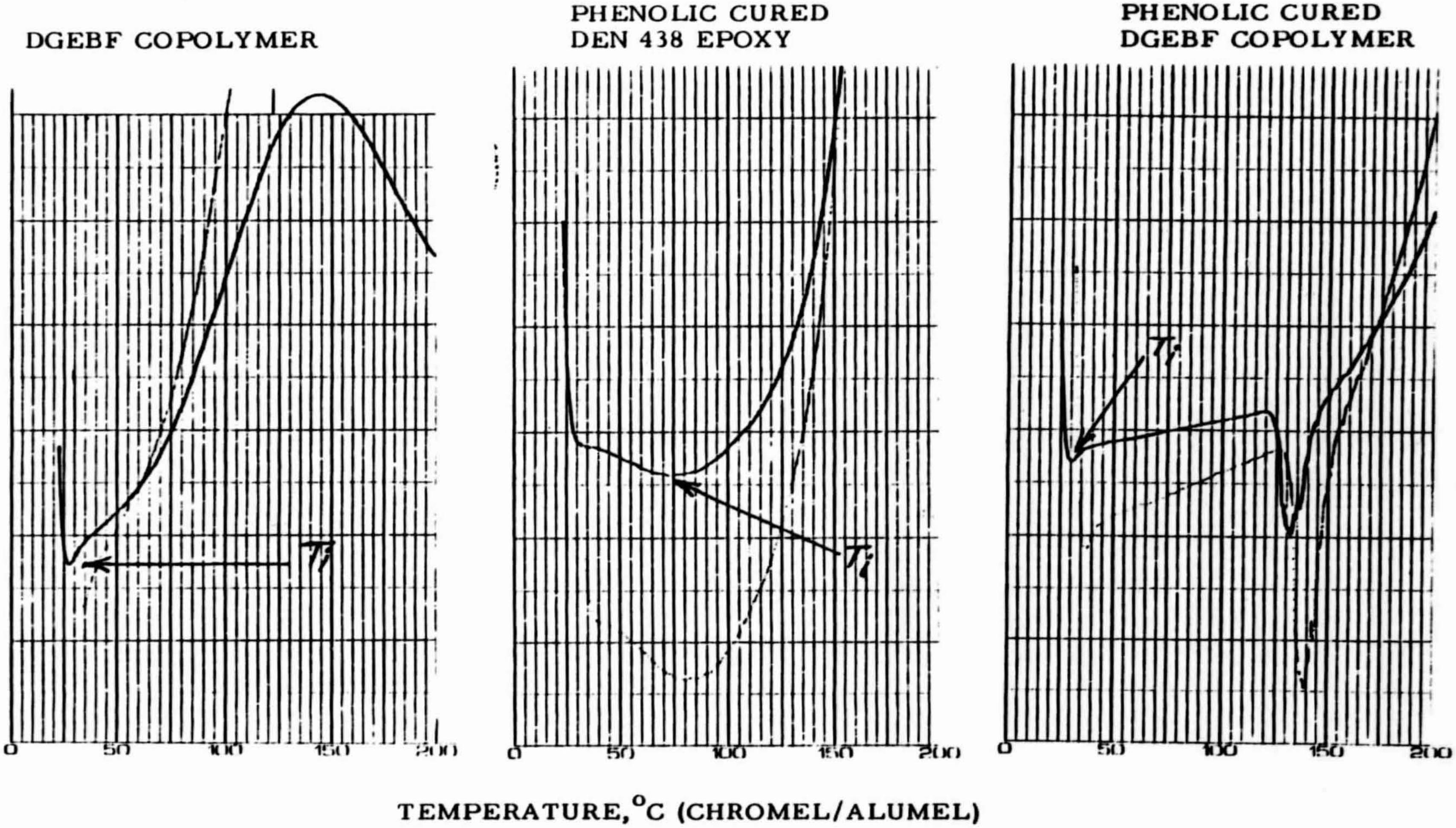


FIGURE 4

GRAPHITE LAMINATE FABRICATION

Fabrication of a graphite laminate using the 25% mol fraction DGEBF copolymer catalyzed with 19 grams of trimethoxyboroxine per epoxy equivalent presents a very basic problem: the limited life of the catalyzed epoxy system precludes normal processing parameters. In making resin specimens for TGA values, this particular copolymer blend changed color at room temperature soon after addition of catalyst indicating reaction was underway.

Several small laminates of 3, 6, and 9 plies were made using a press cure to obtain processing parameters preparatory to making a deliverable graphite laminate. A press cure was chosen over (vacuum/pressure) autoclave cure because the limited life of the graphite prepreg was not firmly established. However, it is estimated to be 2-3 hours. This was determined by placing a section of prepreg in a warm press after standing 2-1/2 hours at room temperature and noting resin flow. Since reaction of the copolymer starts upon addition of the large quantity of catalyst without application of heat, the tentative time frame to complete all operations prior to press cure was established at one hour. The elapsed time for coating 9 plies of graphite cloth and placing in a mold for press cure was 55 minutes. The detailed procedure used to make a successful laminate in a 10" x 12" restrained mold is included in Appendix B. This procedure was developed after examination of a preliminary test laminate. This test laminate was press cured 90 minutes @ 149°C (300°F) and post cured in an unrestrained condition using the following cycle: 3 hours heat up to 177°C (350°F); hold 4 hours at 177°C (350°F); increase heat to 205°C (400°F) and hold for 4 hours; then cool. The result was delamination. To eliminate this delamination the separate post cure was deleted and the cure extended incrementally under pressure to 218°C (420°F).

Physical properties of the DGEBF copolymer graphite laminate 116 mils thick are:

Fiber volume	64.4%	based upon resin sp. g = 1.216
Void volume	1.0%	graphite sp. g = 1.782
Short Beam Shear	8100 psi	
Tg	73°C	

Photomicrographs in Figure 5 at 30X and 100X of a typical cross sectional area confirm the excellent integrity (void free condition) of the laminate. The void volume reported above is a calculated value and does not always represent the quality of the laminate.

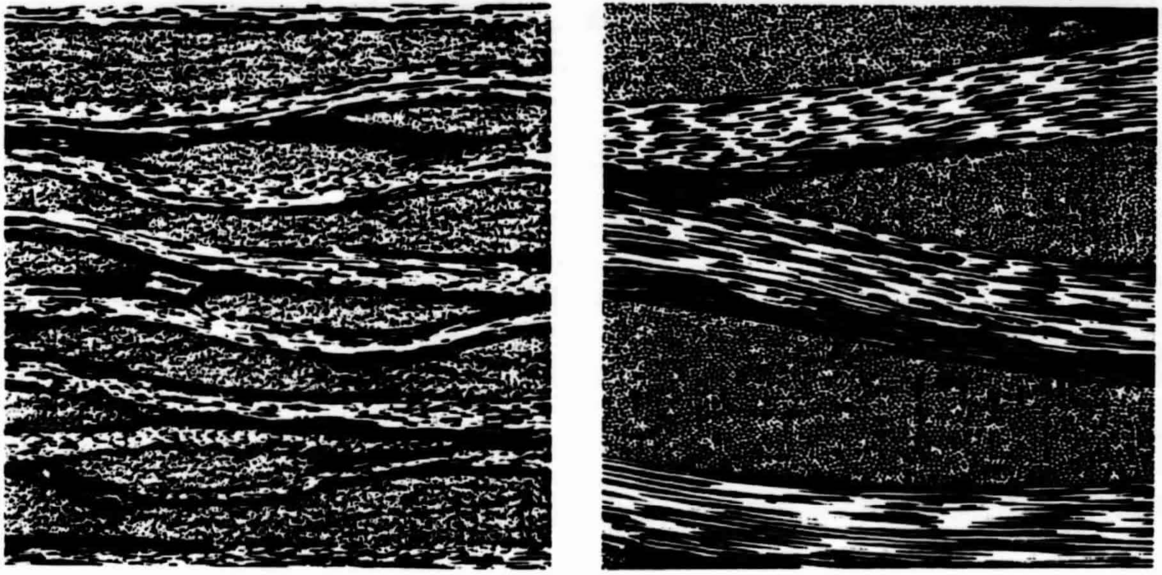


FIGURE 5

In order to make this report more meaningful, two graphite laminates were prepared. One using concepts developed under NAS 2-10207 and a second which combined features of both contracts.

The epoxy phenolic system (DEN 438/BRWE 5833: 20/12) had TGA values of 46.1% & 42.7% at 700°C and 750°C respectively. These are slightly greater than those obtained with the highly catalyzed DGEBF/DGEBA copolymer. Fabrication of the DEN 438/BRWE 5833 resin system graphite laminate was simpler because prepregging was conducted from a solvent system and the resultant prepreg is stable for a period of time. The procedure as outlined in Appendix C for a 9 ply laminate utilizes an autoclave cure which lends itself to commercial production in contrast to the DGEBF/DGEBA procedure.

Physical properties of the phenolic cured epoxy graphite laminate 118 mils thick are:

Fiber volume	62.4%	Based upon resin sp. g. = 1.223
Void volume	0.2%	graphite sp. g. = 1.782
Short Beam Shear	8430 psi	
Tg	105°C	

The photomicrograph at 42X in Figure 6 of a typical cross sectional area confirms the void free condition of the laminate.

FIGURE 6

In order to complete the investigation, a brief evaluation of the DGEBA/DGEBF copolymer cured with BRWE 5833 novalac phenolic which combines the concepts of both contracts was conducted. Based upon 136.5 grams of of copolymer (22.9% mol fraction DGEBF) the following quantities (Table 6) of BRWE 5833 dissolved in methylethyl ketone were used to cure the copolymer. Comparative TGA values for the combination systems cured 2 hours @ 120°C (250°F) and 6 hours @ 160°C (320°F) after removal of MEK under vacuum are listed in Table 6.

Quantity of BRWE 5833	% Char	
	700°C	750°C
84	34.5	32.0
48	30.1	27.0
66	34.2	31.2

TABLE 6

Although the TGA values based upon the limited evaluation were less than 40% and not comparable to the other systems, a laminate was fabricated using solvent prepregging and an autoclave cure. A detailed description of the procedure can be found in Appendix D. The resultant laminate cured at 177°C (350°F) in the autoclave was not fully cured as evidenced by loading of the diamond wheel on trimming. Consequently the laminate was post cured in a press (restrained conditions to preclude delamination) at 75 psi as follows: 5 hours to reach 218°C (425°F), hold for 5 hours at 218°C, and then cool down to room temperature under pressure.

Physical properties of the 110 mil thick laminate are:

Fiber volume	66.8%	Based upon resin sp. g. = 1.223
Void volume	1.3%	graphite sp. g. = 1.782
Short Beam Shear	7280 psi	
Tg	103°C	

The photomicrograph in Figure 7 of a typical cross sectional area at 42X shows the void areas inherent in the laminate. These were not present in the other laminates using the DGEBF copolymer or phenolic cured epoxy.

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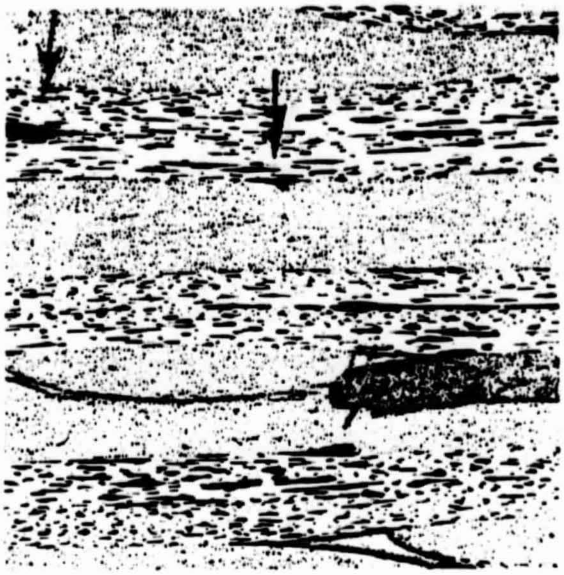


FIGURE 7

CONCLUSIONS

As a result of the copolymer investigation conducted under the NAS2-10130 contract, the following conclusions were established.

1. A properly formulated and processed DGEBA/DGEBF copolymer catalyzed with trimethoxyboroxine will yield char values in excess of 40% at 700°C confirming data reported by Brooklyn Polytechnic.

2. The optimum copolymer for char yield was established at 25% mol fraction DGEBF; however the 19 grams of catalyst (TMB) per epoxy equivalent which equals 8.7% total weight severely limits usable life.

3. A procedure was established for the successful fabrication of 1/8 inch thick graphite laminates using the DGEBA/DGEBF copolymer.

   - The limited pot life and projected cost of DGEBF precludes commercial application.

4. A procedure was established for fabrication of epoxy/phenolic graphite laminates resulting in a cost effective resin system.

   - Readily available commercial materials
   - Stable prepregs from a solvent system provide a procedure suitable for commercial applications.

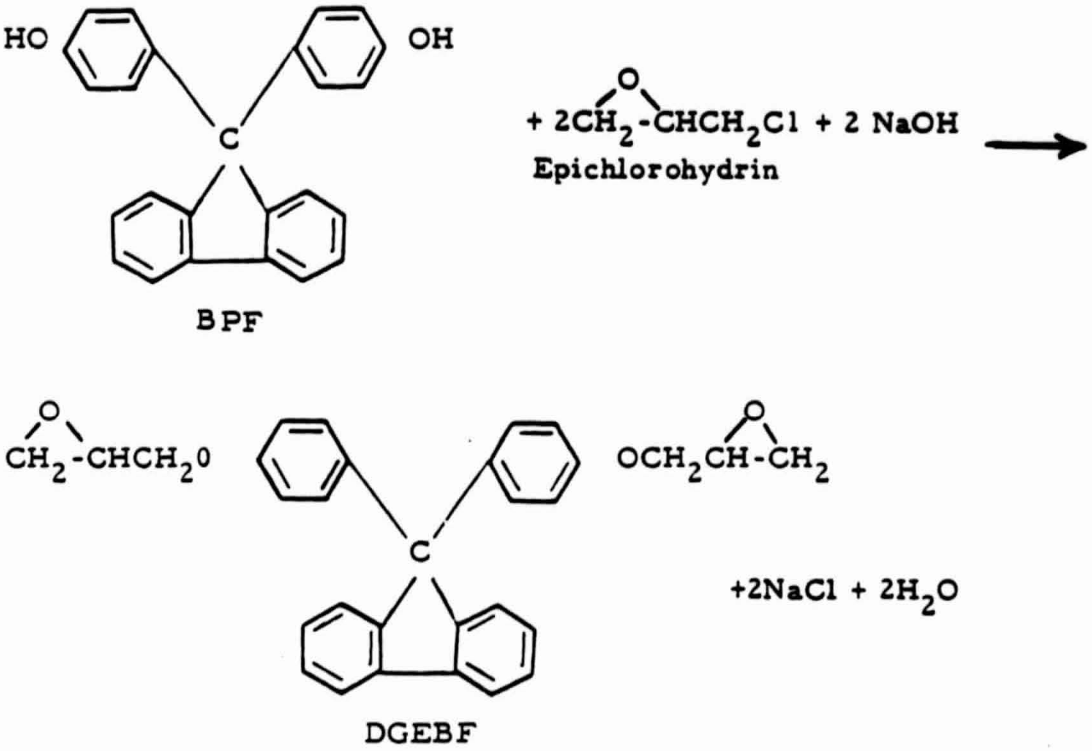
5. Initial evaluation of DGEBA/DGEBF cured with novalac phenolic in a graphite laminate does not seem promising; however optimum cure cycle was not established.

6. Optimum cure cycle including post cure was not established for any high char resin system. The time and funds necessary for such a study were not available.

APPENDIX A

PREPARATION OF DIGLYCIDYL ETHER OF 9, 9-BIS(4-HYDROXYPHENYL) FLUORENE (DGEBF).

Preparation of DGEBF can be represented in an ideal case by the following equation:



In practice the reaction is carried out using an excess of epichlorohydrin to suppress reactions that lead to higher molecular weight products. The resin preparation covered in the following procedure used 5 moles of epichlorohydrin per phenolic equivalent or 10 moles of epichlorohydrin per mole of bisphenol monomer "BPF".

Equipment used in the preparation consisted of a 4 necked glass flask fitted with:

- Stirrer (air driven)
- Dropping funnel
- Thermometer
- Condenser with a phase separating head that returns the lower phase to the flask and permits removal of the upper phase (H_20).

Reactants for a 2-1/2 mol preparation in a 5000 ml flask are:

Bisphenol "BPF"	875 gms	5	equivalents (2-1/2 moles)
Epichlorohydrin	2312.5 gms	25	equivalents (5X excess)
NaOH	224 gms	5.6	equivalents

Preparation

1. Charge the flask with Bisphenol "BPF" and the epichlorohydrin.
2. Prepare NaOH solution (45% by weight) and transfer to dropping funnel. See Note 1.
3. Heat epichlorohydrin/Bisphenol BPF solution to about 100°C.
4. Add 150 millimeters of water to the flask. Contents will now boil at approximately 100°C.
5. Start addition of NaOH solution, adding slowly at the beginning because the NaOH reacts catalytically to initiate the exothermic addition of phenolic groups to the epichlorohydrin.
6. After the initial tendency to exotherm, adjust the rate of NaOH addition and the rate of water removal from the phase separating head to maintain the flask temperature at 102-104°C.
7. After completion of NaOH addition (approximately 2 hours), continue water removal until the flask temperature reaches 120°C and the head temperature 116°C, the boiling point of epichlorohydrin.
8. Cool to approximately 60°C, stir in Celite Filter Aid (John-Manville) and filter the contents to remove the NaCl cake.

9. Transfer the product (filtrate) to a suitable 3-necked flask fitted with a Claisson distillation head, a thermometer and a gas inlet tube through which a fine stream of nitrogen is introduced to stir the flask contents, avoid bumping and aid in the removal of volatile material.
10. Remove bulk of the epichlorohydrin by stripping same under temperature and vacuum. Stripping started at a flask temperature of approximately 50°C and a vacuum of 75 mm Hg.
11. Continue stripping operation down to approximately 15mm Hg and a temperature of 80°C.
12. Reduce vacuum to atmospheric pressure and add 2000 ml of methyl isobutyl ketone and stir. See Note 2.
13. Add 1000 ml of 10% NaOH solution and stir for 60 minutes maintaining a temperature of 80°C.
14. Allow system to separate and remove the lower layer of caustic solution (glass tube, hose and a water aspirator for vacuum).
15. Wash product with 1000 ml of 2% $NaH_2PO_4 \cdot H_20$ solution to neutralize remaining caustic.
16. Add 500 ml of hot water, stir and draw off (See Section 14).
17. Remove methyl isobutyl ketone by distillation under a vacuum.
18. Cool (product crystallizes) and filter
19. Transfer crystalline product to a pyrex baking dish and vacuum dry. Vacuum of less than 200 microns was used.

NOTES

1. Initiation reactions carried out with 5.05 equivalents of NaOH instead of 5.6 resulted in a product with higher than desired hydrolyzable chlorine value (0.5 - 1.0%). The cause was established as chlorohydrin groups left undehydrochlorinated, not epichlorohydrin as initially suspected.
2. In the preparation of the polymer several runs were combined into a 700 gram sample having an average hydrolyzable chlorine value of 1.0%. This sample was reprocessed starting with Step 12.

APPENDIX B

DGEBA/DGEBF RESIN GRAPHITE LAMINATE PROCEDURE

1. Precut 2 pieces of porous TFE coated fiberglass cloth and 16 pieces of bleeder to fit the 10" x 12" mold.
2. Make up 9 batches of resin (30 grams DGEBA (EPON 828), 12.3 grams DGEBF), heat on hot plate until in solution and degas. Do not add catalyst (4.0 grams) at this time.
3. Cut 9 pieces (12 x 14 inches) of graphite cloth furnished by NASA.
4. Align direction of graphite cloth and place on 3/8" aluminum plate heated to 120°F and covered with FEP film.
5. Treating each resin batch separately, warm slightly (∼100°F), add catalyst, stir and degas.
6. Spread catalyzed resin on graphite cloth, cover with FEP film and squeeze out resin.
7. Transfer plate with coated graphite to a heated press (120°F) and squeeze out resin at 40-50 psi pressure making a pre-preg.
8. Repeat 5, 6, 7 for total of nine pieces of graphite.
9. Cut 10" x 12" sections from prepregged graphite using a template.
10. Lay up 9 ply of prepregged graphite warp face to warp face and fill face to fill face.
11. Assemble mold as follows: FEP film, 8 bleeder ply, (TFE porous) cloth, 9 ply stack of "pre-pregged" graphite cloth, porous TFE cloth and FEP film.
12. Place in press at 120°F and hold for 1-1/2 minutes at minimum pressure (actually 3.3 psi); then increase pressure to 75 psi.
13. After 20 minutes total lapsed time, increase temperature to 300°F. Hold 60 minutes; then increase temperature to 350°F. Hold 45 minutes; then increase to 420°F. Hold 45 minutes; then cool to room temperature under pressure.

APPENDIX C

DEN 438/BRWE 5833 RESIN GRAPHITE LAMINATE PROCEDURE

An epoxy novalac phenolic system in methyl ethyl ketone (MEK) having the following formulation was prepared for prepregging graphite cloth.

DEN 438	200 grams	46% solids
BRWE 5833	120 grams	
ETPPI (0.25%)	0.8 grams	
MEK	275 grams	

Prepare above resin system as follows:

1. Dissolve BRWE 5833 in a portion of the MEK
2. Dissolve *ETPPI catalyst in remaining MEK
3. Add solution 2 to solution 1.
4. Dissolve DEN 438 into the catalyzed phenolic solution

*Ethyltriphenyl phosphonum iodide.

Fabricate graphite laminate as follows:

1. Cut 9 pieces of 14" x 14" graphite cloth
2. Place individual pieces of cloth on piece of FEP film, straighten the weave, and pour on resin system. Spread the resin solution with a teflon paddle, thoroughly wetting the graphite cloth.
3. Air dry for 30 minutes after ensuring weave is straight.
4. Force dry for 30 minutes in 150°F oven. Note: coated cloth must be supported while oven drying to ensure straight weave.
5. Cut 12" x 12" sections from the prepregged sheets using aluminum template.
6. Assemble for an autoclave cure as follows:

- Place FEP film on aluminum caul, followed with one layer of bleeder, layer of porous TFE cloth and a 9 ply stack of graphite prepreg laid warp face to warp face and fill face to fill face.

- Cover with a layer of TFE cloth, layer of bleeder, a layer of microporous polypropylene film (Celgard) and FEP film.

- Bag for autoclave cure.

CURE: Apply 22 inches vacuum overnight. Start heat up. At 200°F apply 100 psig pressure. Hold at 350°F for two hours. Turn off heat, allow heat and pressure to decay. At 230°F release pressure and open autoclave door. Remove vacuum at 200°F and continue cool down to room temperature. Remove part.

APPENDIX D

DGEBA/DGEBF/BRWE 5833 RESIN GRAPHITE LAMINATE PROCEDURE

An epoxy copolymer phenolic resin system in MEK having the following formulation was prepared for prepregging graphite cloth.

DGEBA (Epon 828)	100	46% solids
DGEBF	36.5	
BRWE 5833	66	
MEK	238	

Prepare above resin system as follows:

1. Dissolve BRWE 5833 in a portion of MEK
2. Add DGEBF to the Epon 828 and heat to put into solution.
3. Add BRWE 5833/MEK solution to the copolymer.
4. Dilute with remaining MEK to achieve approximately 46% solids.

Fabricate graphite laminate as follows:

1. Cut 9 pieces of 14" x 14" graphite cloth.
2. Place individual pieces of cloth on piece of FEP film, straighten the weave, and pour on the resin. Spread the resin solution with a teflon paddle, thoroughly wetting the graphite cloth.
3. Air dry for 30 minutes after ensuring weave is straight.
4. Force dry for 30 minutes in 150°F oven.
5. Cut 12" x 12" sections from the prepregged sheets using aluminum template.
6. Assemble for an autoclave cure as follows:
   - Place FEP film on aluminum caul, followed with one layer of bleeder, layer of porous TFE cloth and a 9 ply stack of graphite prepreg laid warp face to warp face and fill face to fill face.

- Cover with a layer of porous TFE cloth, layer of bleeder, a layer of microporous polypropylene film (Celgard) and FEP film.
- Bag for autoclave.

CURE: Apply 22 inches vacuum overnight. Start heat up. At 200°F apply 100 psig pressure. Hold at 350°F for two hours. Turn off heat, allow heat and pressure to decay. At 230°F release pressure and open autoclave door. Remove vacuum at 200°F and continue cool down to room temperature. Remove part.